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Laboratory Study of H_2S Reduction in Anaerobic Digester Sludge

by

Renato Chiarella ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

in

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ABSTRACT

Some gases emitted from wastewater treatment plants have become major environmental and operational issues. At the Gold Bar Wastewater Treatment Plant in Edmonton, Canada, hydrogen sulfide produced in the anaerobic digesters can cause corrosion in boilers and an unpleasant rotten-egg-like odor when released to the atmosphere. An effective method to reduce both the formation of odors and corrosion would be through the implementation of chemical precipitation. Reagent grade ferrous and ferric chloride solutions along with a local ferrous chloride waste product were tested to determine which chemical provided the highest degree of hydrogen sulfide removal. The ferrous chloride reagent grade solution and the ferrous chloride waste solution were shown to provide the greatest amount of hydrogen sulfide reduction with respect to dose added. As well, using the local ferrous chloride waste product instead of the reagent grade solution will be an effective method of reducing the chemical cost.

Dedicated to my parents,

ROSARIO CHIARELLA

CATERINA CHIARELLA

For their encouragement, understanding and support.

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LIST OF SYMBOLS

A = Area

c = Mass concentration of liquid phase, where subscript L denotes bulk concentration and subscript I interface concentration

C_f = Hydrogen sulfide mass in floc (mg)

C_b = Hydrogen sulfide mass in bulk liquid (mg)

E = Maximum error of estimate

F = Flux

k = Interface mass transfer coefficient

K_a = Ionization constant

K_f = Floc constant (s^{-1})

K_b = Bulk liquid constant (s^{-1})

n = Size of sample

p = Gas phase concentration, where subscript G denotes bulk concentration and subscript I denotes interface concentration

s = Sample standard deviation

t_α = Area under the t-distribution to its right is equivalent to α (Miller *et al.*, 1990)

t = Time

W = Mass transferred

1. INTRODUCTION

Odor has become an issue of increasing importance in the wastewater treatment industry. Incoming wastewater and byproducts of the wastewater treatment process both contribute to the odor problems associated with wastewater treatment facilities. Many municipalities are facing an increase in public complaints, due to the fact that once isolated wastewater treatment plants are now surrounded by urban development which are subject to unpleasant odors. The odorous gases are also a nuisance to the plant workers, as well as a safety concern, where the hydrogen sulfide gas produced poses a safety issue. This has led municipalities to address the concerns associated with odors through initiating odor control studies. Through recognizing the source of the odor and how it is formed, different control mechanisms can be implemented in order to minimize the odor problem (ASCE and WEF, 1991).

At the City of Edmonton's Gold Bar Wastewater Treatment Plant, problems associated with odors have been encountered throughout the plant. Specifically, anaerobic digesters have been a major source of odorous compounds. The digestion of organic matter through the anaerobic digestion process produces many end products such as methane, carbon dioxide and hydrogen sulfide. The presence of hydrogen sulfide in the digester gases, has led to problems at the Gold Bar Wastewater Treatment Plant that must be solved. First, oxidation of the hydrogen sulfide in the gas stream causes corrosion of the boilers, due to the fact that sulfuric acid is produced upon combustion. Second, the hydrogen sulfide emissions cause an odor problem in the primary sedimentation basin, due to the presence of the gas in the incoming raw sewage and the supernatant which is

recycled to the headworks from the anaerobic digesters. Thirdly, an odor problem also occurs in the lagoons that store the digested sludge. Volatilization of the hydrogen sulfide gas into the air above provides an unpleasant odor to the surrounding area, which can ultimately lead to complaints against the plant. Lastly, a portion of the digester gas is flared into the atmosphere. Thus, emitting hydrogen sulfide and sulfuric acid gas, and contributing to the odor problem. The combination of these problems has stressed the need for the hydrogen sulfide emissions to be controlled.

Reducing the problems related to the hydrogen sulfide gas can be achieved through a variety of methods. In this study, chemical precipitation was the control method specifically researched to diminish the formation of hydrogen sulfide. With the use of metal salts, such as reagent grade ferrous chloride and ferric chloride, hydrogen sulfide levels should be lowered significantly. Along with the latter chemicals, a ferrous chloride waste product was tested to assess its performance relative to the reagent grade chemicals.

With successful results and appropriate application of the chemicals, a reduction in public complaints and a lengthened operating life of the wastewater facility components and structures can be achieved. As well, with the reduction of odorous compounds emitted into the atmosphere, the public perception of the facilities will be improved. Thus, wastewater treatment plants will no longer be viewed as a nuisance by the developed surrounding neighborhood, but will be accepted as part of the community infrastructure.

2. OBJECTIVES

The purpose of this study was to determine the most effective chemical and concentrations required to attain reductions in hydrogen sulfide formation in the anaerobic sludge. The major objectives of this study were as follows:

1. To compare the relative effectiveness of different chemicals (ferrous chloride, ferric chloride and a ferrous chloride waste solution) in reducing the formation of hydrogen sulfide.

2. To establish a relationship between the dose of each chemical added and the hydrogen sulfide reduction attained.

3. To model the mass transfer of hydrogen sulfide in the sludge from one phase to another.

4. To recommend a chemical type and dosage which will provide sufficient reduction of hydrogen sulfide gas formation.

3. LITERATURE REVIEW

3.1 Source of Odors

The odor problem at wastewater treatment plants stems from the decomposition of organic matter in the wastewater, which causes both organic and inorganic gases to be emitted into the atmosphere. Many different offensive odorous compounds exist in untreated wastewater. Typical odorous compounds and their characteristic odors are shown in Table 1. The most prevalent compounds are hydrogen sulfide and ammonia. Many of these gases can volatilize into the atmosphere at different locations in the wastewater treatment plant. These locations include conveyance systems, in system pump stations, primary treatment systems, and sludge processing facilities. Special attention should be given to the pump station, headworks facilities, sludge storage, thickening, stabilization and dewatering facilities (ASCE & WEF, 1991).

Sulfur is a major contributor to the odor problem. Many different types of sulfur compounds can exist in domestic and industrial wastewater. The ionic and molecular inorganic species found at room temperature are bisulfate (HSO_4^-), sulfate (SO_4^{2-}), sulfur (S^0), hydrogen sulfide (H_2S), bisulfide (HS^-), and sulfide (S^{2-}) (Rubin, 1974). Three major groups of organic sulfur compounds create unpleasant odors. These are: 1) the thiols or mercaptans, 2) the thioethers and 3) the disulfides (U.S.EPA, 1974). Each of these species can add to the offensive odors produced and, depending upon the bacteria present, can be reduced or oxidized into different species.

Table 1. Odorous Compounds Associated with Untreated Wastewater (Adapted from Metcalf and Eddy, 1991)

Odorous Compound	Odor, Type
Amines	Fishy
Ammonia	Ammoniacal
Diamines	Decayed Flesh
Hydrogen Sulfide	Rotten eggs
Mercaptans (e.g., methyl and ethyl)	Decayed cabbage
Mercaptans (e.g., butyl and crotyl)	Skunk
Organic sulfides	Rotten cabbage
Skatole	Fecal matter

3.2 Formation of Odors

Wastewater can have differing odors, depending upon whether the wastewater is fresh or has undergone anaerobic decomposition. The most common and characteristic odor of septic wastewater is that of hydrogen sulfide, which can be formed during anaerobic conditions. Anaerobic microorganisms include sulfate reducing bacteria that can reduce the sulfate present in the wastewater to sulfide, which ultimately leads to the production of hydrogen sulfide (Metcalf and Eddy, 1991). This method of bacterial reduction is also referred to as dissimilatory or respiratory sulfate reduction, where the sulfate acts as the terminal electron acceptor. Typical electron donors may include alcohols, fatty acids, and organic acids, however H_2 may also be used as an electron donor by some anaerobic organisms (Mara, 1974, and Higgins and Burns, 1975). Biological reduction of sulfate to sulfide may include the following typical reactions:

$$2CH_3CHOH + SO_4^{2-} \Longrightarrow 2CH_3COOH + S^{2-} + 2H_2O + CO_2 \qquad (1)$$

$$4H_2 + SO_4^{2-} \Longrightarrow S^{2-} + 4H_2O \qquad (2)$$

which illustrates the reduction with different electron donors. Organisms are involved in each of the transformations represented by the reactions in Equations (1) and (2). *Desulfovibrio*, *Desulfomonas*, and *Desulfotomaculum* are the principal organisms involved in reaction (1), and *Desulfobulbus*, *Desulfobacter*, and other organisms are involved in reaction (2) (Brock *et al.*, 1984 and Stanier *et al.*, 1986) (From ASCE, 1989).

Heterotrophic microorganisms can also decompose sulfur-containing organic compounds, where a portion of the sulfur is utilized for cell synthesis and the remaining portion is emitted as hydrogen sulfide. A typical reaction showing the decomposition of an organic compound (methionine) is (Higgins and Burns, 1975):

$$\underset{\text{methionine}}{CH_3SCH_2CHNH_2COOH} + H_2O \Longrightarrow \underset{\text{methyl mercaptan}}{CH_3SH} + NH_3 + \underset{\text{ketobutyrate}}{CH_3CH_2COCOOH} \quad (3)$$

Methyl mercaptan can be converted to methyl alcohol and hydrogen sulfide by biochemical hydrolization according to (ASCE, 1989):

$$\underset{\text{methyl mercaptan}}{CH_3SH} + H_2O \Longrightarrow \underset{\text{methyl alcohol}}{CH_4OH} + \underset{\text{hydrogen sulfide}}{H_2S} \quad (4)$$

3.3 Volatilization of Odors

Several factors such as wastewater pH, total sulfide concentration, temperature, and turbulence conditions can control the volatilization of odorous compounds. The volatilization of the odorous compounds may also be described by Henry's Law and the partial pressure of the odorous gas if the wastewater is not in a closed space and is in equilibrium with the surrounding environment (ASCE and WEF, 1995). Henry's Law states that the saturation concentration of the gas in the liquid is directly related to the partial pressure of the gas above the liquid and the type of gas (Metcalf and Eddy, 1991).

Unfortunately, Henry's Law is valid in ideal conditions which are rarely present in wastewater. Thus, the concentration of odorous gas is more commonly controlled by the rate of sulfide generation, turbulence of the wastewater stream and the air ventilation rates. Turbulence of the wastewater stream can occur in areas that contain Parshall flumes and weirs, where odorous volatile gases are given off at substantially greater rates compared to areas that have quiescent conditions. Wastewater treatment structures such as aeration basins and aerated grit chambers, which release sulfide and organic gases into their surroundings often produce odors (ASCE and WEF, 1995).

3.4 Control Methods

In order to effectively control the odor problems associated with wastewater treatment plants, a proper odor control method should be selected. The three major categories that exist are classified as physical, biological and chemical. The main methods within each class are shown in Table 2.

3.4.1 Chemical Control Methods

Chemicals are commonly added directly to the wastewater, wastewater sludge, or process sidestreams such as supernatants, thermal process decant liquors, and filter backwash waters, which are major sources of odor. As indicated in Table 2, many different chemical methods exist to reduce or eliminate odorous gases. Some chemical methods treat the precursor compounds of the odorous gases (such as HS^- for hydrogen sulfide gas) and others treat the odorous gases after they have formed. Most of the chemical methods are successful in reducing sulfide related odors and corrosion, and a few are successful in treating organic based odors. As with any project, a feasibility assess-

Table 2. Physical, Biological and Chemical Methods to Control Odorous Gases (Adapted from Metcalf and Eddy, 1991, and U.S.EPA, 1985)

Method	Description and/or Application
Physical Methods	
Containment	Using covers or collection hoods to contain odorous compounds. Odors are then conveyed to a disposal or treatment system.
Dilution with odor free air	The strength of odors can be reduced by mixing with fresh air. As well tall stacks can be used to achieve atmospheric dilution.
Combustion	Through combustion, at temperatures from 1200 to 1500°F (650 to 815°C), odors can be eliminated.
Adsorption, activated carbon	Odorous gases can be adsorbed onto the micro and macro pores of the activated carbon. Regeneration of the carbon will reduce costs.
Oxygen Injection	Preventing anaerobic conditions from developing can be achieved through the injection of either pure oxygen or air.
Masking agents	Spraying perfume over objectionable odors can reduce the effect of odorous gases.
Biological Methods	
Trickling Filters or Activated -sludge aeration tanks	Removal of odorous compounds can be achieved by passing the gases through trickling filters, or through activated sludge aeration tanks.
Biological stripping towers	Stripping towers with specially packed media can be used to remove odorous compounds. A biological growth is maintained on the media.
Chemical Methods	
Scrubbing with various alkalies	Scrubbing towers can be used to remove odors. Caustic scrubbers are common.
Chemical Oxidation	One of the most common methods of controlling odors is by oxidizing the odorous compounds. Common oxidants are chlorine, ozone, hydrogen peroxide, and potassium permanganate.
Chemical precipitation	The addition of metal salts is commonly used to remove sulfides from the liquid portion of the wastewater. E.g. ferrous and ferric salts.

-ment should be carried out to ensure that the best treatment method has been selected. For example, chemical addition can sometimes be more beneficial if it is added into the sewerage collection system, rather than the odorous air being scrubbed out at the wastewater treatment plant. If chemical addition to the collection system is not appropriate, chemical treatment can still be effective at the treatment plant for headworks or sludge odor control (ASCE and WEF, 1995).

3.4.1.1 Caustic Absorption Scrubber

A common absorption scrubbing system used in wastewater treatment plants is the caustic scrubber. It is often used to remove hydrogen sulfide from the gas stream by manipulating the pH. Such a system allows the hydrogen sulfide to be scrubbed and transferred to the liquid scrubbant. The sulfide is then removed from the scrubber through an overflow or blowdown stream as shown in Figure 1. Sulfide removal is determined by pH and solubility. Because the solubility of hydrogen sulfide is low (high Henry's Constant) the transfer of hydrogen sulfide gas will only occur if there is a concentration less than 0.01mg/L of molecular hydrogen sulfide in the scrubbant solution. This low concentration of hydrogen sulfide gas is obtained by raising the pH level in the scrubbant solution. Raising the pH causes the ionization of hydrogen sulfide gas to H^+ and HS^- (ASCE and WEF, 1995). Equilibrium water chemistry governs the solubility of sulfide, where sulfide species change as shown in the following relationships (AWWA, 1990):

$$H_2S \Rightarrow H^+ + HS^- \quad ; \quad K_a = 10^{-7} \ (25°C) \qquad (5)$$

$$HS^- \Rightarrow H^+ + S^{2-} \quad ; \quad K_a = 10^{-15} \ (25°C) \qquad (6)$$

where K_a = ionization constant

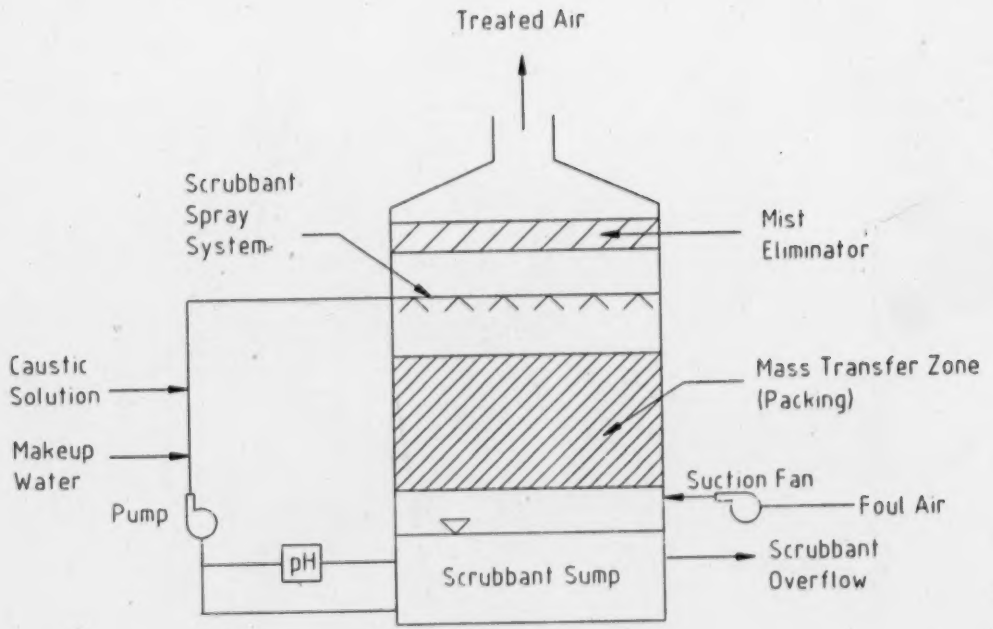

Figure 1. Typical Caustic Absorption Scrubber (Adapted from ASCE and WEF, 1995).

In these relationships the ionization takes place instantly, resulting in the solubility of sulfide increasing with increasing pH, as shown in Table 3. In this type of scrubber a

Table 3. Solubility of Hydrogen Sulfide and Bisulfide Relative to pH

pH	Percentage of H_2S	Percentage of HS^-
1	99.9999	0.0001
2	99.9990	0.0010
3	99.9900	0.0100
4	99.9001	0.0999
5	99.0099	0.9901
6	90.9091	9.0909
7	50	50
8	9.0909	90.9091
9	0.9901	99.0099
10	0.0999	99.9001
11	0.0100	99.9900
12	0.0010	99.9990

minimum pH level of 10 is required to remove the sulfide from the scrubbant. However, levels above a pH of 11 cause calcium carbonate scaling to form on the scrubber packing (depending upon the hardness of the water) (ASCE and WEF, 1995).

3.4.1.2 Chemical Oxidation

Chemical oxidation is another method which is used to control odors at wastewater treatment plants. The strong oxidizing chemicals eliminate the odor-causing compounds through oxidation and reduction reactions. Typical chemical oxidants are chlorine, hypochlorite, hydrogen peroxide, potassium permanganate and ozone. Some of these chemicals contain oxygen in their molecular structure, though their principle function is not to supply oxygen to bacteria, but rather to react with the odorous compounds in the dissolved form (ASCE and WEF, 1995).

Chlorine is commonly used in wastewater treatment plants as a killing agent, as well as to control odorous compounds. Chlorine can exist in many forms: pure gas, hypochlorite solution, or hypochlorite granules or tablets. Whether chlorine gas or hypochlorite solution is used in treating the wastewater, the hypochlorite ion is the reactive component of chlorine. The addition of chlorine solutions may affect the pH of the wastewater, since the hypochlorite is a basic solution and the dissolution of chlorine gas creates an acidic product (ASCE and WEF, 1995).

Chlorine can react with various compounds in raw domestic wastewater, including hydrogen sulfide. Reactions involving chlorine and sulfide are as shown:

$$HS^- + 4Cl_2 + 4H_2O \Rightarrow SO_4^{=} + 9H^+ + 8Cl^- \quad \text{Acidic} \quad (7)$$

$$HS^- + Cl_2 \Rightarrow S + H^+ + 2Cl^- \quad \text{Basic} \quad (8)$$

Any reduced compound in the wastewater is subject to being oxidized by the chlorine and, as a result, overfeeding of chlorine is required to ensure that the sulfide is oxidized. Experience has shown that between 5 and 15 parts by weight of chlorine is needed to oxidize each part of sulfide, depending upon the wastewater characteristics (U.S.EPA, 1985 and ASCE and WEF, 1995).

Chlorine can prevent the formation of odorous compounds by oxidizing the precursor compounds in the liquid phase. As well, it can inactivate or kill numerous types of bacteria that cause odors since it is a strong bactericide. However, because chlorine is non-selective in killing bacteria, the chlorine will also destroy organisms that aid the processes associated with wastewater treatment (ASCE and WEF, 1995).

Hydrogen peroxide (H_2O_2) is commonly used to oxidize hydrogen sulfide to sulfate or elemental sulfur (depending upon wastewater pH). The reactions between hydrogen peroxide and hydrogen sulfide are as follows:

$$H_2S + H_2O_2 \Rightarrow S + 2H_2O \qquad (pH < 8.5) \qquad (9)$$

$$S^{2-} + 4H_2O_2 \Rightarrow SO_4^{2-} + 4H_2O \qquad (pH > 8.5) \qquad (10)$$

Potassium permanganate ($KMnO_4$) is another oxidizing agent that can be used to control odors. When the potassium permanganate reacts with hydrogen sulfide the following reactions take place:

$$3H_2S + 2KMnO_4 \Rightarrow 3S + 2H_2O + 2KOH + 2MnO_2 \qquad (Acidic\ pH) \qquad (11)$$

$$3H_2S + 8KMnO_4 \Rightarrow 3K_2SO_4 + 2H_2O + 2KOH + 8MnO_2 \qquad (Basic\ pH) \qquad (12)$$

Where many different products such as elemental sulfur, sulfate, thionates, dithionates and manganese sulfide may be formed according to these above reactions and several intermediate reactions, depending upon contents of the wastewater. In order for the oxidation of sulfide to occur, practical applications have shown that between 6 and 7 parts of potassium permanganate are required for each part of sulfide present (ASCE, 1989, and U.S.EPA, 1985). Although potassium permanganate can be used in treating odors, it has not been widely used in the United States mainly due to its high cost (ASCE and WEF, 1995).

Ozone is an extremely reactive chemical that is used to oxidize hydrogen sulfide to elemental sulfur. Its principal use has been to control odorous gases, even though ozone reacts with many types of molecules in the wastewater. Such a chemical oxidant is

effective in controlling hydrogen sulfide, though there are no applications showing that ozone treatment is feasible over long-term use (ASCE and WEF, 1995).

3.4.1.3 Chemical Precipitation

Chemical precipitation is a common method to control odors through the addition of metal salts. Because wastewater has high levels of sulfide, in the absence of metals the sulfide reacts with the hydrogen to form hydrogen sulfide. Several studies have shown that the presence of metals in wastewater significantly reduces the levels of H_2S formed. Studies in California have shown that during the 1970's and mid 1980's, there was a rise in H_2S levels in their sewers, leading to greater odor and corrosion problems. This increase in H_2S was attributed to the fact that industrial pretreatment standards were implemented between 1975 to 1977, limiting the amount of metals and toxic materials that could be discharged into the sanitary sewers. Two theories were proposed to explain the increase in sulfide levels and subsequent increase in H_2S levels. The first theory held that the high levels of metals (prior to the pretreatment program) and other toxic constituents were inhibitory to the biological generation of sulfide. The second theory held that the metals and toxic constituents prevented the hydrogen sulfide from being released from the wastewater into the atmosphere of the sewer. This was due to a significant amount of metal-sulfide compounds forming and precipitating out of the wastewater, which prevented the formation of sulfuric acid and subsequent corrosion. While the mechanism is open to debate, this study supported the theory that there was a relationship between decreased levels of hydrogen sulfide and the addition of metals (U.S.EPA, 1991a). Table 4 shows the relationship between the decrease of metals concentrations and the theoretical

stoichiometric increase in dissolved sulfide concentration, after the implementation of the industrial pretreatment standards.

A relatively insoluble metal sulfide will form through the chemical reaction of metals and dissolved sulfides . The black or reddish-brown metal sulfide precipitate does not settle in the sewerage collection system, but does get removed in the wastewater treatment processes. Metal salts such as ferrous and ferric salts can react with hydrogen sulfide which is dissolved in the wastewater (ASCE and WEF, 1995). Laboratory studies

Table 4. Theoretical Increase in Dissolved Sulfide due to the Reduction of Various Metals in LA County (Adapted from U.S.EPA, 1991b)

Metal	Reduction in Metals[a] (mg/L)	Theoretical Increase in Dissolved Sulfide Concentration (mg/L)[b]
Chromium	0.68	0.42
Copper	0.38	0.10
Lead	0.17	0.03
Zinc	1.34	0.66
Nickel	0.14	0.08
Iron	4.92	2.83
Cadmium	0.01	0.00
Total		4.12

[a] Difference in metal concentrations between the periods of 1971 - 1974 and 1983 - 1986
[b] Based on theoretical stoichiometry calculations of chemical precipitation reactions

have shown that optimum results for chemical precipitation have been attained by providing a blend of 1 part ferrous (Fe^{2+}) to 2 parts ferric (Fe^{3+}) (Pomeroy and Bowlus, 1946). This optimum blend of metal salts is not available commercially, thus relatively pure solutions of ferrous and ferric salts are more commonly used in collection systems and treatment facilities (ASCE and WEF, 1995).

Metals such as copper, lead, silver, and zinc can all be used for sulfide control. Although, the concentrations of all four metals in industrial discharges into the collection system and waterbodies are restricted by regulation (ASCE, 1989). Table 5 shows the probable metal - sulfide precipitation reactions in anaerobic wastewater.

Table 5. Some Metal - Sulfide Precipitation Reactions That Can Occur in Wastewater Under Anaerobic Conditions (Adapted from U.S.EPA, 1991b)

Reactions	Theoretical concentration of metal (mg/L) to precipitate 1 mg/L of sulfide
$Fe^{2+} + S^{2-} \Longrightarrow FeS$	1.74
$Zn^{2+} + S^{2-} \Longrightarrow ZnS$	2.04
$Ni^{2+} + S^{2-} \Longrightarrow NiS$	1.83
$Cd^{2+} + S^{2-} \Longrightarrow CdS$	3.51
$Pb^{2+} + S^{2-} \Longrightarrow PbS$	6.48
$Cu^{1+} + S^{2-} \Longrightarrow Cu_2S$	3.97
$Cr^{2+} + S^{2-} \Longrightarrow CrS$	1.63

According to the above, the least amount of iron is required in comparison to other metals (except for chromium) to precipitate 1 mg/L of sulfide. Chromium allows the highest amount of sulfide to be precipitated, though due to its toxicity chromium is not recommended for sulfide control (U.S.EPA, 1991b).

Ferrous and ferric salts are common additives used at treatment facilities for sulfide control. Reactions between ferrous salts and dissolved sulfide produce the same end products, as the anionic carrier of the ferrous ion (chloride, etc.) does not enter the reaction:

$$Fe^{2+} + HS^{-} \Longrightarrow FeS + H^{+} \qquad (13)$$

Ferric salts react in a similar manner when in the presence of dissolved sulfides, where the

following reaction takes place:

$$2Fe^{3+} + 3HS^- \Longrightarrow Fe_2S_3 + 3H^+ \qquad (14)$$

In either reaction, there is a black insoluble ferrous or ferric compound that forms, resulting in the precipitation of sulfide (ASCE and WEF, 1995).

Specific metal salts, such as ferrous and ferric chloride, have been successfully used to control hydrogen sulfide emissions at wastewater treatment plants. Specifically, the San Jose/Santa Clara Water Pollution Control Plant (SJ/SC WPCP) lowered the H_2S concentrations in their digester gas to a target value of 300 ppm through the addition of metal salts. Before chemical additions, digester H_2S concentrations ranged from 2000 to 3000 ppm. A theoretical consideration of the variety of anions that would react with the iron to form sparingly soluble precipitates was considered. When either $FeCl_2$ and $FeCl_3$ are added to the raw wastewater various iron containing solids could form as shown in Table 6.

Table 6. Various Iron Salts That Exist in the San Jose/Santa Clara WPCP Raw Waste Streams (Adapted from Stumm *et al.*, 1981 and Dezham *et al.*, 1988)

Compound	Formula	$-pK_{sp}$	Supersaturated
Ferrous Phosphate	$Fe_3(PO_4)_2$	32	Slightly
Ferrous Sulfide	FeS	18.1	Yes
Ferrous Hydroxide	$Fe(OH)_2$	14.5	No
Ferrous Carbonate	$FeCO_3$	10.4	No
Ferric Phosphate	$FePO_4 \bullet 2H_2O$	26	Yes
Ferric Hydroxide	$Fe(OH)_3$	38.7	Yes

Addition of $FeCl_2$ to the headworks will cause some ferrous iron (Fe^{2+}) to be carried over into the aeration basins of the activated sludge system. In such an environment where there is a supply of oxygen and the pH of the secondary and nitrification mixed liquors are

between 7.1 and 7.6, the oxidation of Fe^{2+} to Fe^{3+} can occur rapidly. Therefore with the addition of $FeCl_2$, there will be a mixture of Fe^{2+} and Fe^{3+} present in the system. With the addition of $FeCl_3$ to the wastewater, again there will some Fe^{3+} carried into the downstream processes. In the reducing environments such as the raw wastewater itself and the primary sedimentation basin, Fe^{3+} will be reduced to Fe^{2+}, again providing a mixture of ferric and ferrous ions (Dezham *et al.*, 1988). Thus, this mixture of iron ions will be more readily available to combine with a variety of anions in the wastewater, to form insoluble precipitates as shown in Table 6.

Preliminary tests provided evidence of the success of chemical precipitation, as shown in Table 7.

Table 7. Primary and Secondary Effluent Concentrations of Soluble Iron at the San Jose/Santa Clara WPCP Before and After Iron Salt Additions (Adapted from Dezham et al., 1988)

	Effluent iron, mg/L	Effluent iron, mg/L
Effluent Type	Before Iron Additions	After Iron Additions
Primary	0.2	0.7
Secondary	0.02	0.07

Prior to any metal salts being added to the raw wastewater, soluble iron concentrations of 0.2 and 0.02 mg/L were observed in the primary and secondary effluents. After adding 1.6 mg/L iron salt (as Fe^{2+}) to the raw wastewater, there was an increase in soluble iron concentration to 0.7 and 0.07 mg/L in these effluents. Therefore, of the 680 kg of Fe^{2+} which were added to the raw wastewater daily at the plant, only 23 kg remained in soluble form in the secondary effluent. Meanwhile, 657 kg of the iron precipitates were stored in the primary and secondary sludges which are conveyed to the anaerobic digesters. In the

digesters, there is a highly reducing environment where the sulfide concentrations are relatively higher in comparison to other anions that form sparingly soluble solids with iron. The combination of both these factors, the high sulfide concentration and the reducing environment allows the sulfide to react with the iron in the sludge which enters the digester. This reaction allows $FeS_{(s)}$ to precipitate out (Dezham *et al.*, 1988).

Further tests were carried out, where $FeCl_2$ was added to reduce H_2S formation. Iron dosages ranged from 1135 to 2770 kg of $FeCl_2$/day. It was found that to meet the H_2S concentration of 300 ppm, the required dose of $FeCl_2$ to the raw wastewater was approximately 3.9 mg/L (Dezham *et al.*, 1988).

Ferric chloride ($FeCl_3$) doses ranged between 3.1 and 6.1 mg $FeCl_3$/L of raw wastewater, which is equivalent to 1360 to 2720 kg $FeCl_3$/day. After experiments were carried out, it was found that approximately 4.4 mg $FeCl_3$/L of raw wastewater was required to meet the target value of 300 ppm H_2S in the digester gas. Therefore, experimental data indicated that a lower dose of $FeCl_2$ (3.9 mg/L) was required in comparison to $FeCl_3$ (4.4 mg/L). As well, the cost of $FeCl_2$ was less than that of $FeCl_3$. Thus $FeCl_2$ was selected for permanent use at the water pollution control plant (Dezham *et al.*, 1988).

The optimal point of $FeCl_2$ addition was investigated. Initially, $FeCl_2$ was added directly into the digester feed/recirculating sludge line. H_2S concentrations were effectively controlled, but a vivianite (ferrous phosphate) scale formed inside the piping and plugged the system. Prevention of the vivianite scaling was accomplished by adding the $FeCl_2$ directly to the headworks, instead of the digester feed/recirculating sludge line.

The minor alteration did not have any detrimental effect on the primary, secondary, or tertiary treatment efficiencies to remove SS, BOD_5 or ammonia. Increases in the primary and secondary effluent iron concentration were observed as shown in Table 7. Overall, $FeCl_2$ additions provided adequate control over H_2S concentrations with minimal operational drawbacks (Dezham *et al.*, 1988).

A permanent dosing station (which included a storage tank, metering pumps and piping) was constructed for approximately $30 000, and annual costs for $FeCl_2$ averaged $220 000 per year or $1.20 per 1000 m^3 of wastewater treated. All are in 1987 U.S. dollars (Dezham *et al.*, 1988).

In another study, high concentrations of hydrogen sulfide emissions from the Los Angeles County anaerobic digesters were also controlled through chemical precipitation. Dissolved metals were added to the digested sludge in order to form metal precipitates. Iron was used because it was relatively inexpensive and high concentrations of the iron could be tolerated in the anaerobic digester. Specifically, ferrous chloride ($FeCl_2$) was added to the digester, and provided substantial control over the hydrogen sulfide concentrations in the digester gas (ASCE, 1989). The addition of $FeCl_2$ has significantly diminished the H_2S emitted, where concentrations were consistently kept below 400 ppm. Meanwhile there has been no noticeable change in alkalinity, pH, gas production or volatile acid concentration, allowing the digester to function as normal (ASCE, 1989).

3.4.2 Biological Control Methods

The use of biological systems for foul air treatment is common in the wastewater industry. Typical processes from which odorous air is collected for treatment are grit

chambers, primary clarifiers, thickeners, screen room, and vacuum pumps (U.S.EPA, 1985).

Microorganisms in the wastewater treatment processes are responsible for the production of hydrogen sulfide and other odorous compounds through their metabolic activity, yet other microorganisms can metabolize these odorous compounds into nonodorous forms. Many factors govern the performance of biological systems, as stated in Table 8. If one or more of these factors are not applied properly, the performance of the biological system can be inhibited (ASCE and WEF, 1995).

Table 8. Factors Affecting Biological System Performance
(Adapted from ASCE and WEF, 1995)

1.	Transfer of odorous compounds from the gas phase to the liquid phase or to the surface of a solid allowing access to microorganisms
2.	Availability of oxygen to ensure aerobic conditions
3.	Moisture Content
4.	Temperature
5.	pH
6.	Carbon food supply for microorganisms - found within media, carbon dioxide and odorous compounds
7.	Nutrients for microorganisms
8.	Age of the biological system
9.	Biological system must be operated and maintained properly
10.	Foul air stream must be applied uniformly

3.4.2.1 Wastewater Trickling Filters

Wastewater trickling filters at treatment plants can serve to treat odorous compounds, as well as primary and secondary effluent. Treatment can occur by transporting the foul air from areas such as covered headworks and primary clarifiers, where the air is pumped to the bottom of the trickling filter. The air is then recycled from the top of the covered filter to the bottom, where a portion of the recycled stream is

pumped to a mist scrubber for final treatment. Loading the wastewater trickling filter in this manner allows the oxidation of approximately 60% of the hydrogen sulfide. Oxidation occurs by the absorption of hydrogen sulfide and other odorous compounds into the biological slime layer, containing a variety of microorganisms that developed on the media material (ASCE and WEF, 1995). Sulfide that is absorbed into this slime layer is oxidized to either elemental sulfur and/or sulfate, depending upon the oxidizing bacteria that are present.

3.4.2.2 Activated Sludge Systems

Odorous gases can be used as process air for activated sludge aeration tanks, in order to remove odorous compounds (Metcalf and Eddy, 1991). Studies conducted in Japan have shown that aromatic hydrocarbons and dimethyl sulfide, which were the primary odorous compounds in a gas stream, were removed at a level of better than 90%. In another gas stream where hydrogen sulfide and ammonia were prevalent, both compounds were removed at a level between 96 and 100%. These studies support the fact that the activated sludge system can be an effective mechanism to treat odorous compounds in air (Fukuyama *et al.*, 1986).

Transportation of the foul air to the activated sludge system must be given careful consideration. An economical approach would be to feed the foul air into the blower intakes, though the ducting must be resistant to the corrosive effects of the hydrogen sulfide and moist air. Such a treatment system will only be effective if the system is not overloaded and a satisfactory dissolved oxygen concentration is maintained in the aeration

system. Therefore an existing activated sludge system should be carefully studied prior to treating odorous compounds, in order to prevent deterioration of the activated sludge system (ASCE and WEF, 1995)

3.4.2.3 Biofilters

Biofilters have generated a lot of attention in the odor control industry, since they do not require a large use of chemicals. Biofilters consist of soil, peat, compost and similar bulk media. These natural media provide ideal conditions for bacteria to thrive, allowing for the removal of 90 to 99% of biodegradable air pollutants in odorous gas streams (Bohn and Bohn, 1986). Two mechanisms allow the biofilters to remove odorous compounds: absorption/adsorption and biooxidation. First, the odorous gases pass through a biofilter, and are absorbed into the moist surface layer of the biofilter media particles and/or are adsorbed onto the surface of the particles. Biodegradable components of the odorous gases are then metabolized by microbial flora which are commonly found in soils and compost. The biological oxidation process involves microorganisms such as bacteria, actinomycetes and fungi (ASCE and WEF, 1995). Maintaining an appropriate moisture level in the media for the bacteria to thrive can be accomplished through installing spray nozzles above the filter. The pH of the filter media must also be maintained, since in the presence of hydrogen sulfide the bacteria produce sulfuric acid which lowers the pH of the media (Vaith *et al.*, 1996)

3.4.2.4 Bioscrubbers

Bioscrubbers operate in a manner similar to biofilters, with the exception that there is a continuous recirculation of water around the bioscrubber. Both systems are very

economical due to their low operating costs, however the area required by the biofilter can be large. Overall, the removal efficiency of odorous compounds is better for biofilters in comparison to bioscrubbers, though fluctuations in the composition of the odorous gases or flowrate can inhibit the effectiveness of biofilters (Mills, 1995).

In a bioscrubber, the media consist of high-porosity, wet scrubbing packing materials, instead of the soil, peat, compost materials usually found in biofilters. The recirculating liquid flows over the packing material and absorbs contaminants from the odorous air in the biofilter. A thin slime layer, which contains bacteria, develops on the packing material. The bacteria convert the contaminants into various compounds, for example volatile sulfur compound contaminants are converted into sulfuric acid (Morton *et al.*, 1996).

Research was conducted in the Los Angeles County Sanitation District in order to optimize the growth of sulfur oxidizing bacteria, such as thiobacillus. In the presence of hydrogen sulfide (the energy source for the bacteria) and oxygen the bacteria can produce sulfuric acid:

$$H_2S + 2O_2 \xrightarrow{\text{Bacteria}} H_2SO_4 \qquad (15)$$

With the production of the sulfuric acid byproduct, the acid concentration in the recirculation solution must be monitored, because the solubility of the hydrogen sulfide in the water decreases as the acid concentration of the solution increases. Sulfur oxidizing bacteria can withstand pH levels below 1.0, although to satisfy the growth of the bacteria and the solubility of hydrogen sulfide in the water pH levels should be between 2.0 to 3.0. In order to neutralize the acid and ensure an adequate pH, the recirculation water can be

diluted with inlet wastewater. Advantages of this hydrogen sulfide control method over other control methods include: low operational costs, minimal labor requirements, and no chemical additions (Morton *et al.*, 1996).

3.4.3 Physical Control Methods

Many physical methods exist to control odors, as shown previously in Table 2. Two major methods are adsorption and oxygen injection. Adsorption occurs when odorous molecules adsorb to the surface of bulk solid media, such as silica gels, activated alumina impregnated with potassium permanganate or activated carbon. (ASCE, 1989). Oxygen injection can prevent the formation of odors, by increasing the amount of oxygen in the water and preventing anaerobic conditions.

3.4.3.1 Adsorption

Adsorption is commonly used in the treatment of odorous gases (U.S.EPA, 1985). Through adsorption, molecules are adsorbed into the fissures on the surface of the adsorbate. Activated carbon is highly selective in eliminating organic gases and vapors from the gas stream due to its non-polar nature, where the physical and chemical characteristics of the odorous compound determine the amount adsorbed by the carbon (National Academy of Sciences, 1979). Various factors govern the amount of adsorbate that can be adsorbed by the activated carbon as shown in Table 9.

Activated carbon unfortunately has a limited lifespan, and the carbon must be replaced regularly or regenerated. With continued use, the pores on the carbon become filled, and thus the activated carbon reaches its adsorptive capacity and its ability to control odors is diminished. Reactivation of the carbon can be carried out through heating

Table 9. Factors Governing Adsorption (Adapted from U.S.EPA, 1985)

1.	Concentration of compounds surrounding the activated carbon
2.	Surface area of the activated carbon
3.	Volume of micro and macropores
4.	Temperature
5.	Presence of other contaminants competing with compounds specifically to be absorbed
6.	Molecular weight, boiling point, polarity, size, and shape of the compounds to be adsorbed
7.	Contact time of the odorous compounds within the activated carbon packing

the used carbon to 930°C and passing steam through it (ASCE, 1989). A typical activated carbon filter unit is illustrated in Figure 2.

Activated carbon's ability to adsorb hydrogen sulfide can be increased by impregnating the carbon with potassium hydroxide or sodium hydroxide. Regeneration must occur by rinsing the impregnated carbon and then placing it in a chemical solution of concentrated hydroxide. Unfortunately, the chemical regeneration will primarily remove sulfur compounds, leaving other compounds to accumulate in the carbon. Therefore, impregnated carbon must eventually be regenerated with heat to remove the non-sulfur compounds, or it must be replaced altogether (ASCE, 1989).

3.4.3.2 Oxygen Injection

An effective method to prevent anaerobic conditions and control odors in a wastewater collection system is through the addition of oxygen. Most odor production in wastewater can be prevented if a dissolved oxygen concentration of at least 1.0 mg/L is maintained at all times (U.S.EPA, 1985 and ASCE, 1989). Often odors are produced in collection systems because an insufficient amount of dissolved oxygen is available. Adding oxygen to a system will provide a means of reducing and/or preventing the formation of

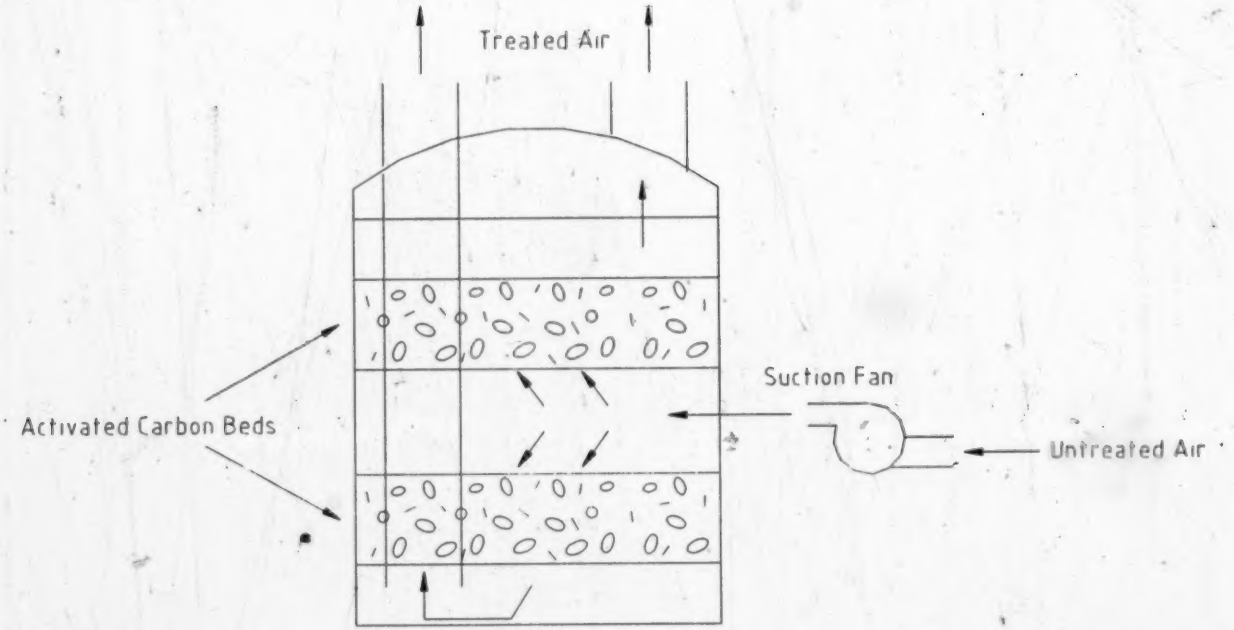

Figure 2. Typical Activated Carbon Filter Unit (Adapted from U.S.EPA, 1985).

odorous compounds. Oxygen addition may oxidize odor causing compounds directly or may provide aerobic bacteria with sufficient oxygen to oxidize odor causing compounds through a metabolic process. Typical applications of oxygen addition include air injection and pure oxygen injection (ASCE and WEF, 1995). Since the prevention of odors occurs through the presence of bacteria and chemical reactions, oxygen injection may also be considered a biochemical method of reducing odors.

Air injection has been used successfully in gravity sewers and force mains. With the injection of air into such areas the dissolved oxygen concentration of the wastewater can be improved, thus preventing the formation of sulfides downstream from the injection point and aid in the oxidation of existing sulfides to sulfate or sulfur as shown in the following reactions:

$$H_2S + 2O_2 \Rightarrow 2H^+ + SO_4 \qquad (16)$$

$$2H_2S + O_2 \Rightarrow 2H_2O + 2S \qquad (17)$$

Air can also be used to control odors. Though the solubility of oxygen from air in water at normal pressures is low and the release of residual gases can occur. This release may carry with it odors from the wastewater, due to the odorous compounds diffusing into the undissolved air. Along with diffusion of odorous compounds, turbulence may also increase the release of odors. Pure oxygen injection has a definite advantage over the addition of air. Due to the difference in partial pressure, five times more pure oxygen will dissolve in wastewater than will the oxygen in air, thus reducing the volume of gas that must be pumped into the wastewater to achieve the same mass of oxygen transfer. Pure oxygen injection has also led to reductions in BOD_5 levels, reducing the required level of

treatment downstream (ASCE and WEF, 1995). Typical locations that can benefit from oxygen injection include hydraulic falls, force main discharges and drop manholes.

3.5 Review of Corrosion

The most common type of corrosion is oxidation which, with iron, results in the formation of rust. The oxidation process occurs due to the exchange of electrons between the free oxygen available in the environment and the metal that is present. This leads to the formation of metal oxides, which are more electrochemically stable than the initial metal present. Therefore, the rate of reaction is inhibited due to the formation of the oxide on the metal surface. Further corrosion can be prevented by oxide barriers such as with chromium, aluminum and nickel. However, other oxides, such as iron oxide, may be porous or subject to chemical attack by chlorides, sulfates and other wastewater constituents making them an ineffective barrier (WPCF Manual of Practice, 1969).

Throughout the wastewater collection and treatment processes, various corrosive chemicals such as chlorine, acids and alkalis are commonly used. As well, sewage treatment process byproducts, such as sludge supernatant liquors can be extremely corrosive. Numerous gases such as H_2S and SO_2 can also be corrosive, either after their reaction with water and oxygen or in the gaseous state (WPCF Manual of Practice, 1969)

Many different materials and components, such as concrete and ferrous sewers, electrical contacts, and copper pipe, can be subject to corrosion when the hydrogen sulfide is oxidized. This oxidation process leads to the formation of sulfuric acid,

$$H_2S + 2O_2 \xrightarrow{\text{Bacteria}} H_2SO_4 \qquad (18)$$

where the acid will attack most materials present. In general, two basic mechanisms cause corrosion by hydrogen sulfide: 1) acid attack from the sulfuric acid formed from the biological conversion of hydrogen sulfide; and 2) the direct attack by hydrogen sulfide gas on metals such as copper, iron and steel. Corrosion of sewers and structures which are used in the transportation and treatment of wastewater is mainly due to mechanism 1. Whereas corrosion of copper pipe, electrical contacts and other metal components are caused by mechanism 2. Considering concrete pipes, the microbe *thiobacillus* causes sulfuric acid to be formed at the crown of the pipe (U.S.EPA, 1991a). The acidic conditions cause the cement bonding materials to be attacked, which results in a pasty mass of gypsum ($CaSO_4$) being created. Yet, the aggregate is unharmed by the acid conditions, since it is virtually inert. The weakening of the cement causes the aggregate to fall into the wastewater and exposes a new layer of cement to corrosion. On the other hand, a ferrous pipe suffers corrosion due to direct attack on the metal. The H_2S can react with most metal pipes, such as iron pipes, and destroy them with continued exposure to H_2S (ASCE, 1989).

In a wastewater treatment plant, equipment must also be protected from exposure to H_2S. Various equipment and components such as steel tanks, structural members, gratings and walkways, grit collectors, bar screens, and conveyers can all be corroded (U.S.EPA, 1985). As well, instrumentation and electrical equipment containing materials such as copper and silver will be subject to corrosion if H_2S exists in the air. Thus, actions must be taken to prevent contact of metals with H_2S laden air (ASCE, 1989).

Structures and components at wastewater treatment facilities will experience the most severe corrosion when subjected to fluctuations between dry and wet conditions and changes in ambient temperatures. When iron and steel are submerged in wastewater the rate of corrosion will be slower, since a protective iron oxide film forms on the surface. However, if the iron or steel is exposed to the atmosphere, the protective iron oxide coating will fall off and expose the underlying surface, allowing further corrosion to take place. Water can also cause corrosion, as it can act as an electrolyte when salt is present. The hydrolization of paint components by water may reduce the adhesion and strength of the coating. As well, a lower resistance of the coating may be observed, allowing the passage of gases such as oxygen and H_2S, which may cause corrosion of the underlying surface. Other problematic materials include, oils, greases, and soaps, which can accumulate at the waterline of aeration tanks, holding tanks, and wet wells. These materials contain solvents which may cause softening of the paint or coating, thus decreasing the resistance of the protective layer (U.S.EPA, 1985).

Enclosed structures such as wet wells, grit and screen chambers, holding tanks and enclosures for wastewater or sludge processing equipment are subject to corrosion due to the moist atmosphere and corrosive gases such as H_2S. Moisture condenses on the cold surfaces of the structures and absorbs oxygen and other gases which can potentially result in a corrosive condensate. The moist atmosphere may also pose physical stresses upon the paints and coatings due to changes in moisture and temperature, which can result in the destruction of the protective film (U.S.EPA, 1985).

When considering the anaerobic digesters at Gold Bar Wastewater Treatment Plant, a major issue is the corrosion of the boilers using digester gas. The oxidation of the hydrogen sulfide in the boilers forms sulfuric acid, which corrodes the boiler tubes, and reduces the useful life of the boiler. The formation of sulfuric acid through combustion is shown in the following three reactions:

$$2H_2S + 3O_2 \Longleftrightarrow 2H_20 + 2SO_2 \qquad (19)$$

$$2SO_2 + O_2 \Longleftrightarrow 2SO_3 \qquad (20)$$

$$SO_3 + H_2O \Longleftrightarrow H_2SO_4 \qquad (21)$$

The H_2SO_4 condenses on the boiler tubes and causes severe corrosion, leading to their replacement approximately every six months. Therefore, the formation of hydrogen sulfide gas in the digesters must be controlled to prevent such expensive operational problems from occurring in the boilers or the hydrogen sulfide must be removed before the gas is burned.

3.6 Anaerobic Digestion

The natural decomposition of organic matter by bacteria has been an ongoing process for millions of years. The decomposition of organic matter such as grass, leaves, animal waste and refuse results in the production of nutrients which are returned to the soil. This process is carried out by bacteria and fungi, which are responsible for breaking down the material biologically. Some forms of bacteria thrive in any environment, though others require certain environmental conditions to carry out their work. Bacteria use the available organic material as food, digesting it and releasing end products consisting of gases, liquids and stabilized solids. Bacterial decomposition can occur either aerobically or anaerobically. Bacteria that require oxygen are called aerobic bacteria, others that thrive in the absence of oxygen are called anaerobic bacteria. Bacteria that can live in either an aerobic or anaerobic environment are called facultative bacteria. Containing anaerobic microorganisms in a digester enhances the rate of decomposition of organic matter. Thus their use in wastewater treatment plants is widespread (U.S.EPA, 1976).

3.6.1 Digestion of Organic Matter

3.6.1.1 Aerobic or Anaerobic?

Two major types of digestion exist, aerobic and anaerobic digestion. Aerobic digestion is fairly uncommon in comparison to anaerobic digestion, mainly due to its relatively high operating cost, high energy demands, and inability to recover energy through the production of a burnable gas (U.S.EPA, 1976). For the digestion of sanitary sludge, anaerobic digestion has been a popular choice among environmental engineers.

Table 10 states the advantages of stabilizing sludge through the process of anaerobic digestion.

Table 10. Advantages of Anaerobic Digestion Processes (Adapted from Lettinga, *et al.*,1979)

1.	High organic loading rates can be handled through a high degree of waste stabilization
2.	Nutrient requirements are low
3.	No aeration equipment is required
4.	A burnable gas in the form of methane is produced
5.	Minimal deterioration of sludge will occur if unfed for a period of one year
6.	May be less sensitive to toxic compounds compared to aerobic processes

3.6.1.2 Removal of Organic Matter

Wastewater from sanitary sewers contain two main types of wastes, where approximately 70 percent is classified as organic and 30 percent inorganic. The organic portion is used as food by the anaerobic bacteria, though the inorganic portion passes through the anaerobic treatment steps unchanged. Fortunately many of these inorganics, such as rocks, grit, rags, plastics metal, etc., are removed by the pretreatment stage. Any materials passing through the pretreatment stage maybe classified as either settleable, suspended or dissolved. The settleable solids are removed in the primary settling tanks and are referred to as raw primary sludge. The suspended and dissolved solids move on to the next stage of the treatment, which is the secondary treatment process. During the biological treatment process the dissolved and suspended solids are converted to biological solids. These solids settle out in the secondary clarifier, and are transferred to the anaerobic digester to be degraded (U.S.EPA, 1976). A schematic of the above processes is shown in Figure 3. The Gold Bar Wastewater Treatment Plant also uses all of the processes shown in Figure 3. An aerial view of the plant is shown in Figure 4.

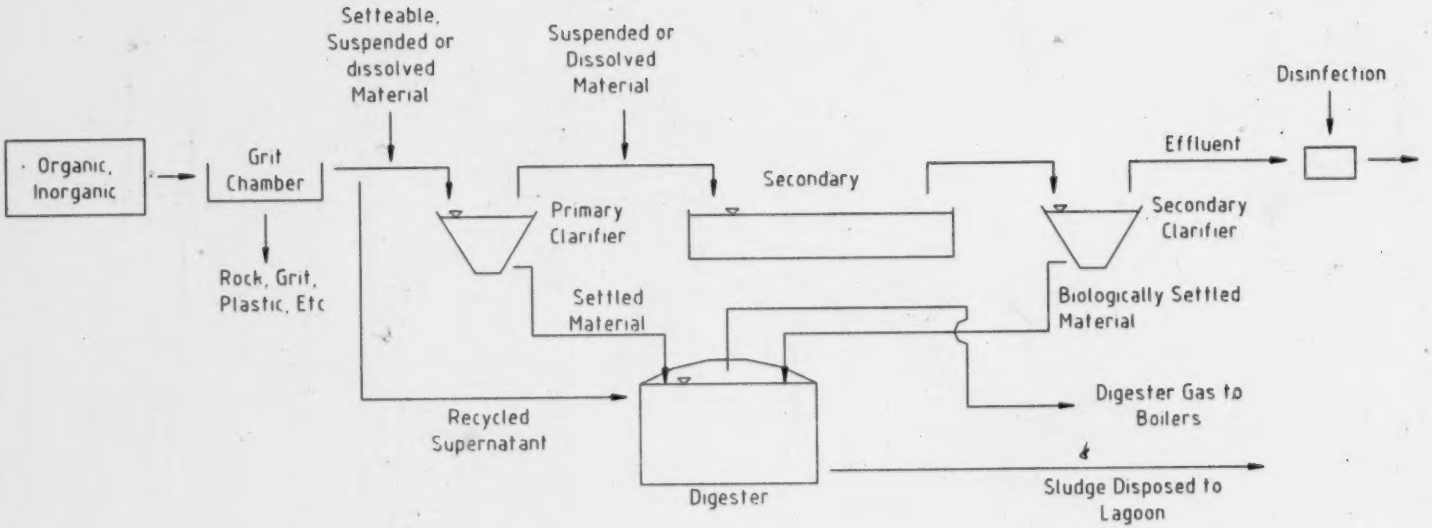

Figure 3. Schematic of Materials Removed From Wastewater.

Figure 4. Aerial View of the Gold Bar Wastewater Treatment Plant.

3.6.2 Metabolic Activity and Environmental Factors

3.6.2.1 Metabolic Activity

The metabolic activity of the anaerobic reactor population must be properly maintained, in order for the complete degradation of the organic matter to methane, carbon dioxide, hydrogen sulfide and other products to occur. Generally, the anaerobic sludge digestion process can be considered in three simple steps. In the first step hydrolyzation occurs, transforming higher molecular mass compounds into simpler compounds. The simpler compounds (shown in Figure 5) are used as a source of energy and cell carbon. Step two involves bacteria, usually referred to as acid formers, degrading the simple compounds into organic acids (McCarty, 1964b, McCarty, 1966 and Holland *et al.*, 1987). The third step involves bacteria, referred to as methanogens, converting the hydrogen and acetic acid formed in the second step to methane and carbon dioxide (Higgins *et al.*, 1975 and Holland *et al.*, 1987) All of these phases, which are shown in Figure 5, are required for the sludge to be stabilized.

In the second stage, the important consideration is the type of food made available to the acid forming bacteria. Food may be classified as either insoluble or soluble. Insoluble food, such as fats, oils, or complex solids are not easily broken down. However, the insoluble food can be broken down by enzymes which are produced by bacteria, thus enabling the solubilized solids to be consumed. The soluble solids, on the other hand, can be used directly by the bacteria. Therefore solids must be in the soluble form for consumption, as only soluble solids can pass through the cell wall of the bacteria. Once in the cell wall, the cell membrane allows soluble organic and metabolic wastes in and out of

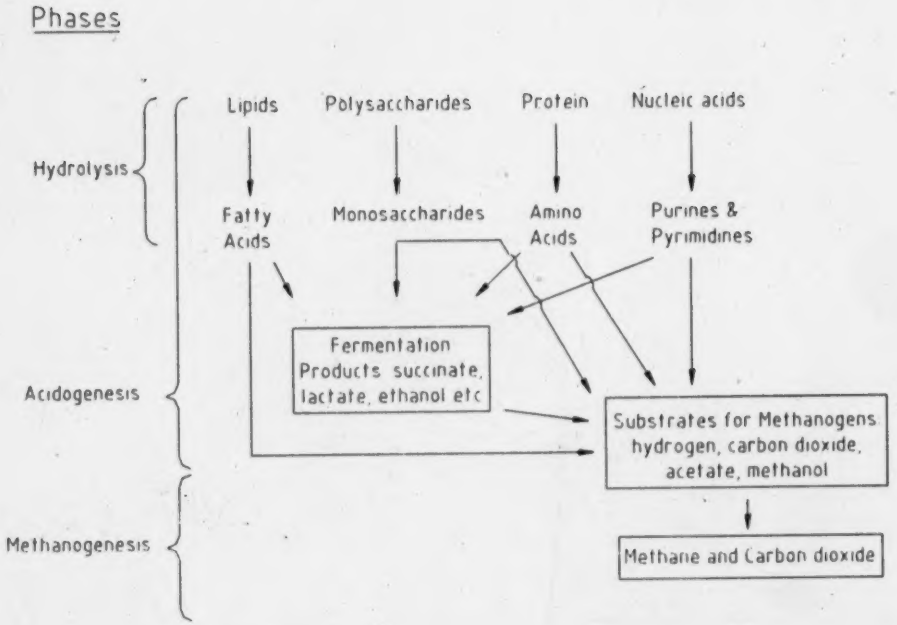

Figure 5. Phases of Waste Stabilization (Adapted from Holland et al., 1987).

the inner cell. Some of the organic solids are not broken down, leading these materials to be part of the non-degradable portion of the digested sludge. This non-degradable material is referred to as the inert solids, which cannot be used as food for the bacteria (U.S.EPA, 1976).

When methane and carbon dioxide have been formed, the waste is said to be stabilized. Two principal reactions are involved in the formation of methane:

$$4H_2 + CO_2 \overset{\text{bacteria}}{<==>} CH_4 + 2H_2O \qquad (22)$$

$$CH_3COOH \overset{\text{bacteria}}{<==>} CH_4 + CO_2 \qquad (23)$$

In equation 22, hydrogen and carbon dioxide are converted to methane and water, and in equation 23, acetate is converted into methane and carbon dioxide (Metcalf and Eddy, 1991). To provide an efficient stabilization process, the methane formers must be provided with an agreeable environment. Factors such as organic loading, pH, temperature and anaerobic conditions must all be considered in the design of an anaerobic digester, as methane formers are very sensitive to slight changes in these factors. On the contrary, acid forming bacteria are not as sensitive to environmental changes (U.S.EPA, 1976).

3.6.2.2 Temperature

One of the major factors influencing anaerobic digestion is temperature. Proper control of temperature will enhance the viability of the bacteria, where a mesophilic temperature range of 25 to 45°C is suggested for the operation of an anaerobic digester. An ideal temperature for the growth of anaerobic microorganisms is approximately 35°C, though some digesters have been operated at 20°C. Such a low temperature will allow

anaerobic growth, but the growth rate is diminished and problems in the startup of some digesters have been reported. If any anaerobic digester is to be operated at low temperatures, the start up will be greatly aided if the temperature is initially at 35°C (Stronach *et al.*, 1986). Temperatures below 10°C severely inhibit the activity of the bacteria, and although the bacteria are unharmed, they will continue to have a very low metabolic rate until the temperature rises (U.S.EPA, 1976).

The methane forming bacteria are very sensitive to changes in temperature as little as 0.6°C, although the acid formers which are responsible for the second stage of sludge stabilization are not as sensitive to changes in temperature. Thus, with temperature changes there may be a continuous formation of acids, while a reduced activity of the methane formers occurs. This may cause instability within the anaerobic digester, as the buffering capacity and pH may be reduced. Thus, a constant temperature is recommended which will allow optimum bacterial activity to occur. If there are problems in keeping the digester at a temperature of 32 to 36°C, as could be the case in a northern location, it is better to operate the digestion at a constant lower temperature. Attempts to increase the temperature will be inhibiting to the bacteria if the higher temperatures cannot be maintained (U.S.EPA, 1976). Therefore, the temperature should be continuously monitored, to help provide an optimum environment for the bacteria to thrive. The anaerobic digester sludge at the Gold Bar Wastewater Treatment Plant is maintained at a temperature of 37°C.

3.6.2.3 pH and Volatile Acids

The hydrogen ion concentration, characterized by pH, is another important parameter that governs microbial metabolism. Proper pH adjustment leads to the optimal growth of microorganisms, where a satisfactory pH range is 6.4 to 7.4. This range is set to satisfy the requirements of both the acid and methane formers. The acid formers can function at pH values above 5, though activity of the methane formers is inhibited by pH values below 6.2. Therefore, the pH is constantly kept above 6.2 to accommodate the methane formers. An optimum pH range is 6.8 to 7.2. This provides good conditions for both the acid and methane forming bacteria (U.S.EPA, 1976). The anaerobic digester sludge at the Gold Bar Wastewater Treatment Plant is maintained at a pH between 7.1 and 7.3.

The amount of volatile acids and the alkalinity in the digester have a strong correlation with the pH of the digester. The amount of sludge fed into the digester affects the amount of organic acids produced. In a normally functioning anaerobic digester, methane formers consume the organic acids at the same rate at which they are produced. The acids are produced by the consumption of the organic matter (food) by the acid forming bacteria. Thus, if a consistent amount of sludge is added to the digester, a balance occurs between the amount of acids produced and consumed. If there is a sudden addition of sludge into the digester, a large amount of organic acids will be produced, thus leading to a lower pH in the digester. This low pH will inhibit the methane forming bacteria, creating a larger buildup of organic acids in the digester. This alteration in pH can be prevented by ensuring high alkalinity in the digester, which provides good buffering

capacity. Therefore, to provide optimal conditions for the degradation of organic matter, pH, volatile acids production and alkalinity must all be monitored constantly (U.S.EPA, 1976).

3.6.3 Operation of an Anaerobic Digester

3.6.3.1 Bacteria and Food

The concentration of bacteria in a digester will influence the digestion of organics. Bacteria act as the "workers" in the digestion process resulting in the production of stabilized sludge. The operator of the digester must make sure that there is always a sufficient amount of seeding available. Seeding is defined as the active solids from a properly maintained and healthy digester. Guidelines suggest that there should be approximately 20 times more seed sludge present than feed sludge, when expressed as volatile solids. Food for the bacteria will be provided by the organic material in the primary and waste secondary sludges. Raw primary sludges produce the clearest supernatant where the sludge is easily dewaterable. In contrast, biological sludges (from the secondary clarifier) do not produce good quality supernatant. Some wastewater treatment plants choose to separate the primary and secondary sludges, where the primary sludges are treated through an anaerobic digester and the secondary sludges in an aerobic digester in order to improve overall plant performance (U.S.EPA, 1976).

3.6.3.2 Loading

For the proper design of an anaerobic digester, the organic and hydraulic loading factors have to be considered. Organic loading is defined as the mass of volatile solids (food) that are fed to the digester on a daily basis per unit volume of digester. Hydraulic

loading is defined as the volume of sludge per unit time entering the digester with respect to the total volume of the digester. This design parameter must be considered, as there is a minimum time requirement for the digester to stabilize the sludge. Depending on the type of digester and solids added, the hydraulic loading will vary. A high rate system may require residence times as low as 10 days, where as a single unheated unit may require up to six months. Wastes, such as pure domestic wastes, require short periods of time for decomposition, though municipal wastes which contain cellulose (added by an industry) need an extended period of time. Food processing industries which operate on a seasonal basis, may produce a problem due to the increased amount of sludge produced. An overload may occur in the system, where lime or other such caustics may need to be added to increase buffering capacity (U.S.EPA, 1976).

3.6.3.3 Contact

In order to produce a stable sludge, bacteria must be mixed (contacted) with the food. Mixing will allow for the bacteria to be exposed to the maximum amount of food, help speed up the breakdown of the volatile solids, and aid in the increased production of gas (U.S.EPA, 1976).

The process of mixing the sludge can be accomplished through two methods, gas production and recycling and mixing devices. Gas, which form pockets that eventually rise to the surface, is produced through the digestion process. By the gases rising to the surface, a boiling effect occurs in the digester resulting in the production of some turbulence. This method of gas production is controlled through the feeding process, where a constant loading will cause internal mixing. If loading is kept at this rate, no other

mixing is required, though low loading for long periods of time may interrupt the mixing process allowing scum blankets to form on the surface. Increased loading can cause organic overloads, which can also cause the rate of gas production to be decreased (U.S.EPA, 1976).

The digesting sludge may also be stirred or mixed by artificial means. Internal fixed mixers are a common method used for the mixing process where steam, digester gas or hot gas is pumped into the sludge. Again, the rising gas bubbles cause turbulence in the sludge, providing good contact. Internal mechanical mixers also provide good mixing through the use of propellers, impellers and turbine wheels, where the sludge is physically moved by the turning motion. All these mixing methods will bring about good contact of the bacteria and the food, which will result in sludge stabilization (U.S.EPA, 1976).

At the Gold Bar Wastewater Treatment Plant, mixing in digesters 1 to 4 is provided by draft tube mixers and in digesters 5 to 6 it is provided by biogas cannon mixers. In both cases, gas is passed through the mixers. In the draft tube mixer, gas pockets are emitted from the bottom of the tube that eventually rise to the surface of the digester sludge. In the biogas cannon mixer a large blast of gas is conveyed through the mixer, producing a large gas pocket which rises to the surface of the sludge. This mixer theoretically provides a greater amount of turbulence in the sludge. In all the digesters, some mixing is also provided by the heat exchangers that heat the sludge. A Diagram of digesters 1 to 4 is shown in Figure 6, respectively. Digesters 5 and 6 are similar to digesters 1 to 4, with the exception of the draft tube mixers being replaced with biogas cannon mixers.

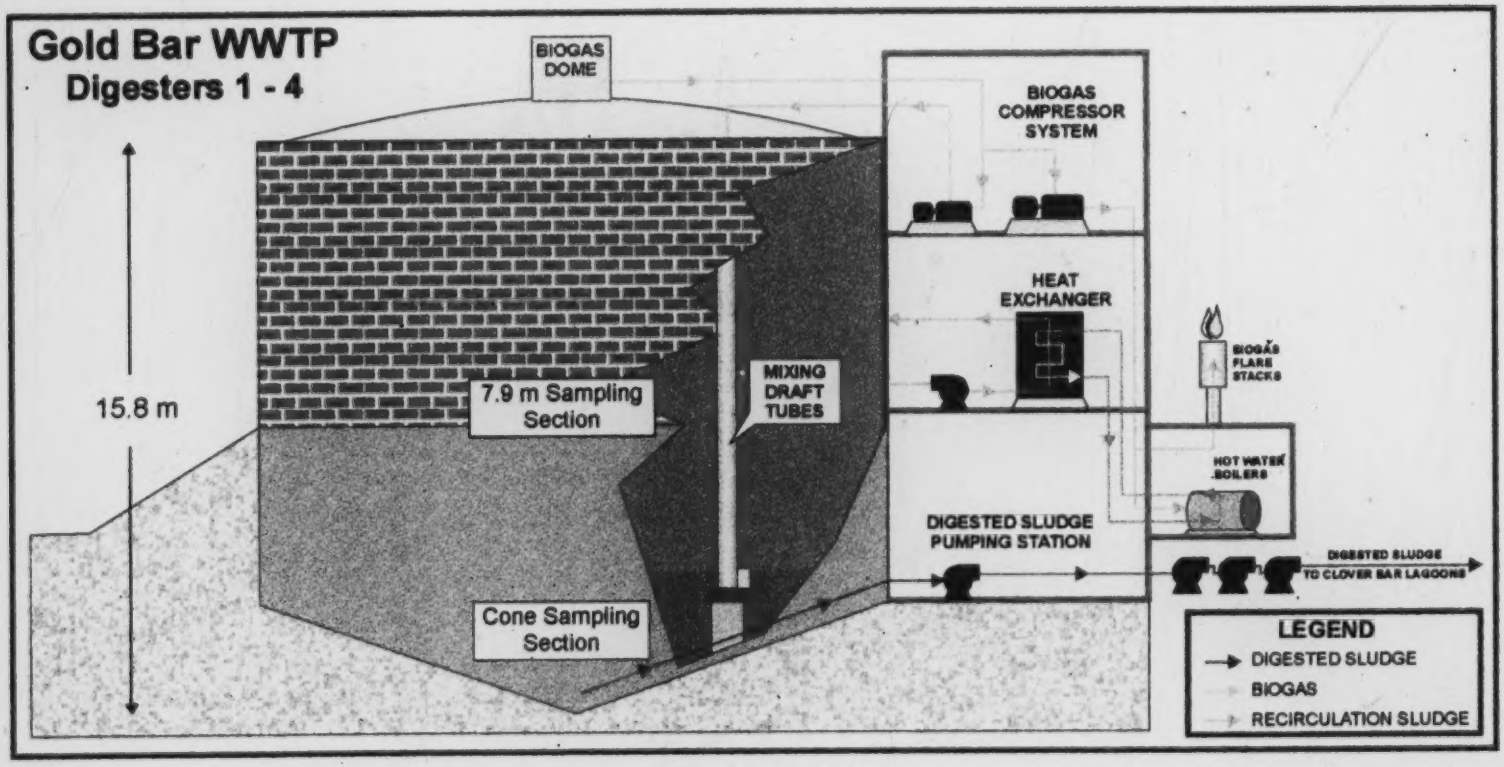

Figure 6. Schematic of Digesters 1 to 4 at the Gold Bar Wastewater Treatment Plant (Drawn by Robert Chamberlain, Gold Bar WWTP Operator).

3.6.4 Types of Anaerobic Digesters

A variety of facilities exist for the anaerobic digestion of sludge. Different types include standard rate, single stage high-rate, and two stage digesters. In the standard rate digestion process the sludge is digested in one single stage. There is no artificial mixing in the tank, though heating of the sludge is provided by heat exchangers. As the sludge is digested, stratification of the sludge takes place. Scum, supernatant, and sludge layers form. Digestion occurs only in the sludge layer in the middle to lower levels of the digester, thus no more than 50 percent of the volume of the digester is used. Due to these limitations, standard rate digesters are generally used in smaller applications (Metcalf and Eddy, 1991).

Single stage high rate digesters offer a more efficient digestion process as compared to the standard rate digestion method. A major difference between the two is that the solids loading rate is much higher in the high rate digester. As well, the sludge is mixed by artificial means such as gas recirculation, mechanical mixers, pumping or draft tube mixers. Due to the intimate mixing, no supernatant layer develops. As well, the total solids in the incoming sludge is reduced by 45 to 50 percent and converted to end products (Metcalf and Eddy, 1991).

In two stage digestion, two tanks are coupled in series. The first tank is used for the digestion of the sludge, where adequate mixing and heat is provided. The second tank allows storage and stratification of the sludge into a concentrated sludge layer and supernatant layer.

At the Gold Bar Wastewater Treatment Plant, the anaerobic digestion process most resembles that of high rate digestion. There are a total of 6 digesters at the plant, where digesters 1 to 5 have a sludge capacity of 6 ML each and digester 6 a capacity of 9 ML. The sludge from the primary tanks is pumped to the digesters, with a 4 to 6 percent solids concentration. The sludge has an approximate detention time of 17 days in each digester, after which it is conveyed to the Clover Bar lagoons.

3.6.5 Gases Produced

Through the anaerobic digestion process various gases are formed. Approximately 65 to 70 percent of the total gas volume is methane, 25 to 30 percent is CO_2, and the remaining volume consists of N_2, H_2, H_2S, water vapor and other gases. Relative to air, the digester gas has a specific gravity of 0.86. The production of digester gas can be used as a measure of the progress of the digestion process. Methane is commonly used as a fuel in wastewater treatment plants, which stresses the need for familiarization of the amount and type of gases produced (Metcalf and Eddy, 1991).

Chemical additions to the anaerobic digestion process can potentially contribute to reduced gas production. Previous studies have shown that chemical coagulants, such as alum and ferric chloride (commonly used in the removal of phosphorus in wastewater treatment) can lead to reduced methane production. The addition of alum and ferric chloride to wastewater produce sludges that, when digested anaerobically, cause a reduction in the amount of methane produced Concentrations of aluminum up to 144 mg/L have caused reduced levels of methane gas, which could be due to the organics being trapped in the resulting flocs. The trapped organics are not easily accessible to the

acid forming bacteria, resulting in the inhibition of the methane forming bacteria. Experiments carried out with ferric chloride have shown similar results, where floc formation has contributed to reduced methane generation (Kindzierski, 1984).

3.6.6 Toxic Materials

Toxic materials must be soluble and in solution for the digester process to be inhibited or completely ceased. Some potentially toxic materials are shown in Table 11.

Table 11. Stimulatory and Inhibitory Concentrations of Toxic Materials in Anaerobic Digestion (Adapted from Kugelman and McCarty, 1964 and Kugelman and McCarty, 1965 and McCarty, 1964a)

	Stimulates	Moderately Inhibits	Strongly Inhibits or toxic
Na (mg/L)	100 to 200	3500 to 5500	8000
K (mg/L)	200 to 400	2500 to 4500	12000
Ca (mg/L)	100 to 200	2500 to 4500	8000
Mg (mg/L)	75 to 150	1000 to 1500	3000
NH_3 -N (mg/L)	50 to 200	-	1500 - 3000[a]
Soluble S^{2-} (mg/L)	-	-	200

[a] Inhibits the anaerobic digestion process at high pH values

Heavy metals in significant concentrations, as well as toxic organics, can inhibit or be toxic to the digester bacteria. Domestic wastes rarely contain concentrations of heavy metals or toxic organics high enough to cause problems in anaerobic digesters. However, failure can occur if industries discharge appreciable amounts of industrial wastes into the sewer system (Kindzierski, 1984).

Toxic heavy metals can include copper, zinc, and nickel. High concentrations of such metals in the absence of sulfates can inhibit or cause total failure of the digestion process. If sulfates are present, they will be reduced to sulfides resulting in the formation and precipitation of insoluble metal salts. Such a reaction, will render the heavy metals non-toxic (Lawrence and McCarty, 1965). If sulfates are not present, the metals will

adversely affect the acid and methane forming bacteria, resulting in lower volatile acid concentrations and gas production (Lawrence and McCarty, 1965). The effect of heavy metal toxicity on gas production is shown in Table 12.

Table 12. Relationship Between Heavy Metal Toxicity and Gas Production (Adapted from Lawrence and McCarty, 1965)

Heavy Metal Added	Heavy Metal Additions (Days)	Gas Production (% of Control)	Methane Content in Gas (%)
Copper (397 mg/L)	13	69	60
	20	24	50
Zinc (409 mg/L)	5	83	67
	13	5	50
Nickel (367 mg/L)	5	81	67
	13	22	67

High iron concentrations in anaerobic digesters have been found to be non-toxic to digester bacteria. Concentrations of 1396 mg/L have been found to inhibit the process slightly, where a small decrease in gas production was observed. High levels of iron can be tolerated since the iron is minimally toxic, and the precipitation of iron as the hydroxide by hydrolysis prevents toxic levels of iron from remaining in the sludge. The hydrolysis of iron will result in a lower pH in the digester, thus more buffering materials will need to be added (Lawrence and McCarty, 1965). Conclusions based on tests carried out on various heavy metals are shown in Table 13.

Table 13. Conclusions of Tests Conducted with Copper, Zinc, Nickel and Iron on the Anaerobic Process (Adapted from Lawrence and McCarty, 1965)

1.	Soluble heavy metals such as copper, zinc and nickel can be toxic to anaerobic treatment, unless precipitated out by an equivalent concentration of sulfides.
2.	The presence of high concentrations of iron in the digester can be tolerated, if the iron is added with the incoming feed sludge.
3.	There is a direct relationship between the amount of toxic heavy metals which can be tolerated and the amount of sulfides present.
4.	Adding sulfide or sulfide precursors is an acceptable method of reducing digester toxicity due to heavy metals.

4. METHODS AND MATERIALS

4.1 Quality Control and Assurance

The quality of the experimental results are directly related to the experimental procedure. In order to ensure that the results attained are valid, all the possible variables which can affect the results must be investigated and taken into consideration when developing the experimental procedure. An efficient experimental protocol was developed by determining the appropriate value or type of six variables: the pH of the sludge, scrubber solution concentration, helium flowrate, stripping time, diffuser type and mixing rate.

A procedure was developed to remove hydrogen sulfide from 0.5 litre samples of anaerobic digester sludge. The experimental setup consisted of four reactors. Each contained a diffuser, magnetic stir bar, teflon valve for chemical additions, and 0.5 litres of sludge. A tank of pre-purified helium, supplied by Praxair Products Inc., Edmonton, Alberta, was connected to all four of the reactors. The pressurized helium would flow through a spherical stone fine bubble diffuser, emitting fine bubbles to purge hydrogen sulfide and other anaerobic gases from the sludge. The sludge gases are conveyed to an impinger containing NaOH, enabling any available hydrogen sulfide in the sludge gas stream to be captured. Details of the experimental setup are shown in Figures 7 and 8.

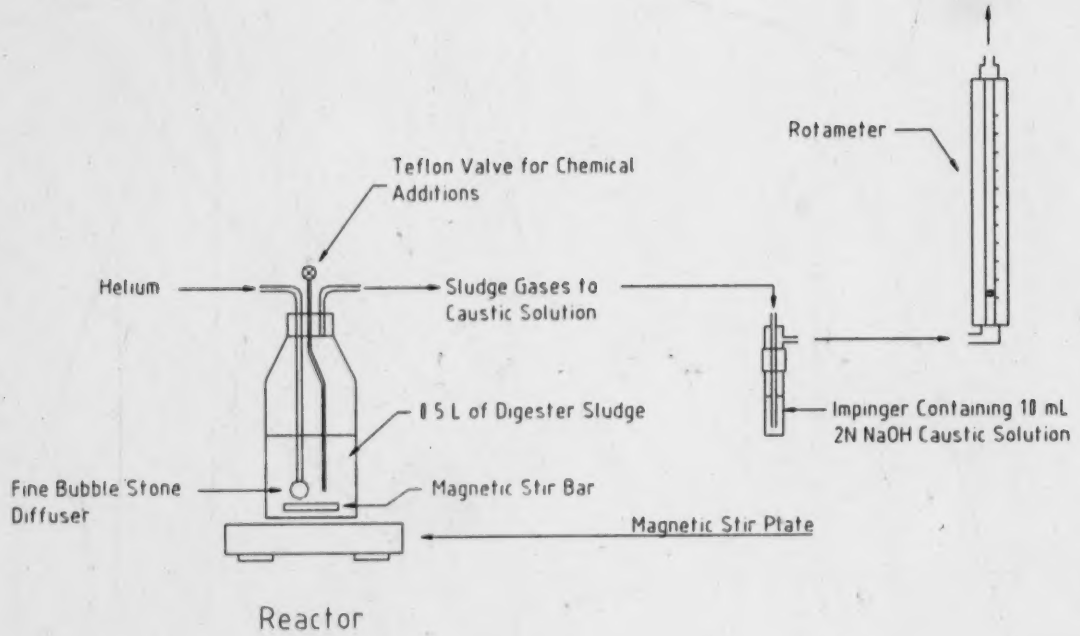

Figure 7. Experimental Setup for Each Reactor.

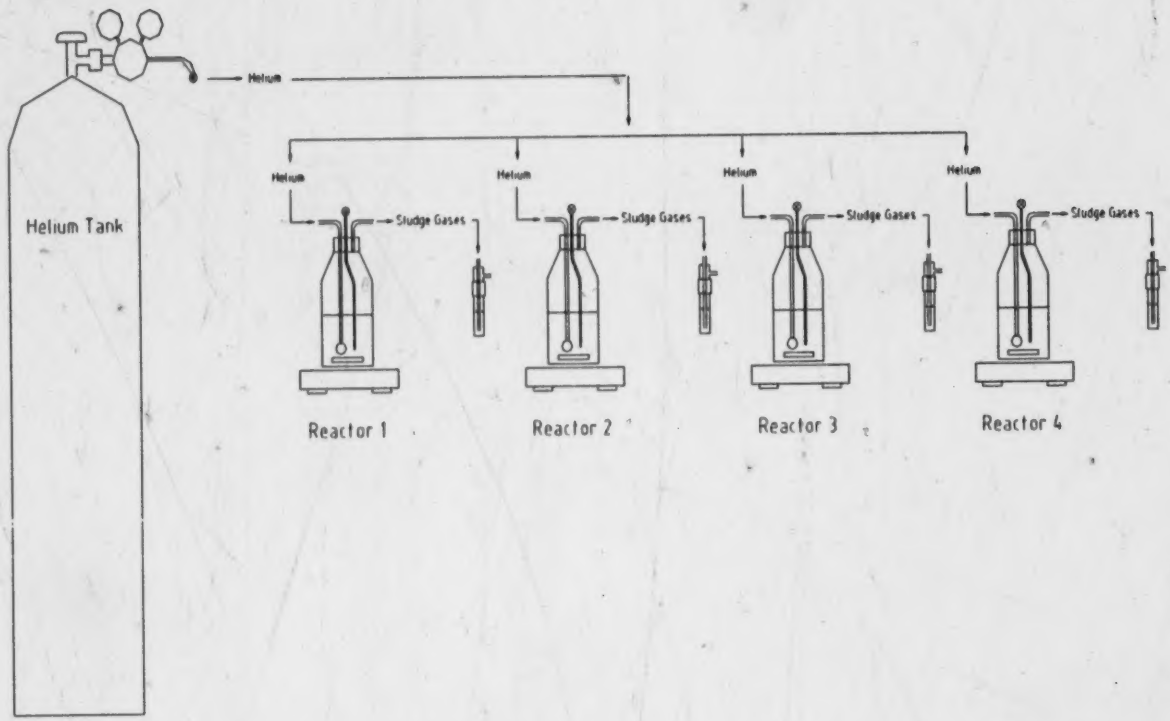

Figure 8. Complete Experimental Setup.

4.1.1 Altering pH of Sludge

The pH can be lowered to efficiently remove the greatest amount of hydrogen sulfide out of any liquid. Lowering the pH causes any available sulfide or bisulfide to be converted to hydrogen sulfide, as shown in Figure 9. This is also shown by the following equilibrium reactions (AWWA,1990):

$$H_2S + H_20 <=> H_30^+ + HS^- \quad K_1 = 1 \times 10^{-7} (25°C) \qquad (24)$$

$$HS^- + H_20 <=> H_30^+ + S^{2-} \quad K_2 = 1 \times 10^{-15} (25^OC) \qquad (25)$$

The following formula can be used to calculate the percent of total sulfide that exists as hydrogen sulfide at a certain pH at equilibrium:

$$\%H_2S = \frac{100(H^+)^2}{(H^+)^2 + K_1(H^+) + K_1K_2} \quad , \qquad \text{where pH = -Log } (H^+) \qquad (26)$$

Experiments were performed to determine the effect of adjusting sludge pH on H_2S recovery. An Accumet model 50 pH meter, supplied by Fisher Scientific, was used throughout the experiments to analyze the pH of the sludge and other solutions. Table 14 shows that adjusting the sludge pH to slightly above 2 allows a significantly higher amount of hydrogen sulfide to be stripped out of the sludge. However, sulfide compounds in the solid form may be dissolved as pH is decreased. For instance, if the pH is lowered by adding acid to the sludge, any metal sulfides present can be dissolved leading to greater amounts of hydrogen sulfide being removed. Thus, the addition of acid will overestimate the amount of hydrogen sulfide available in the liquid portion of the sludge.

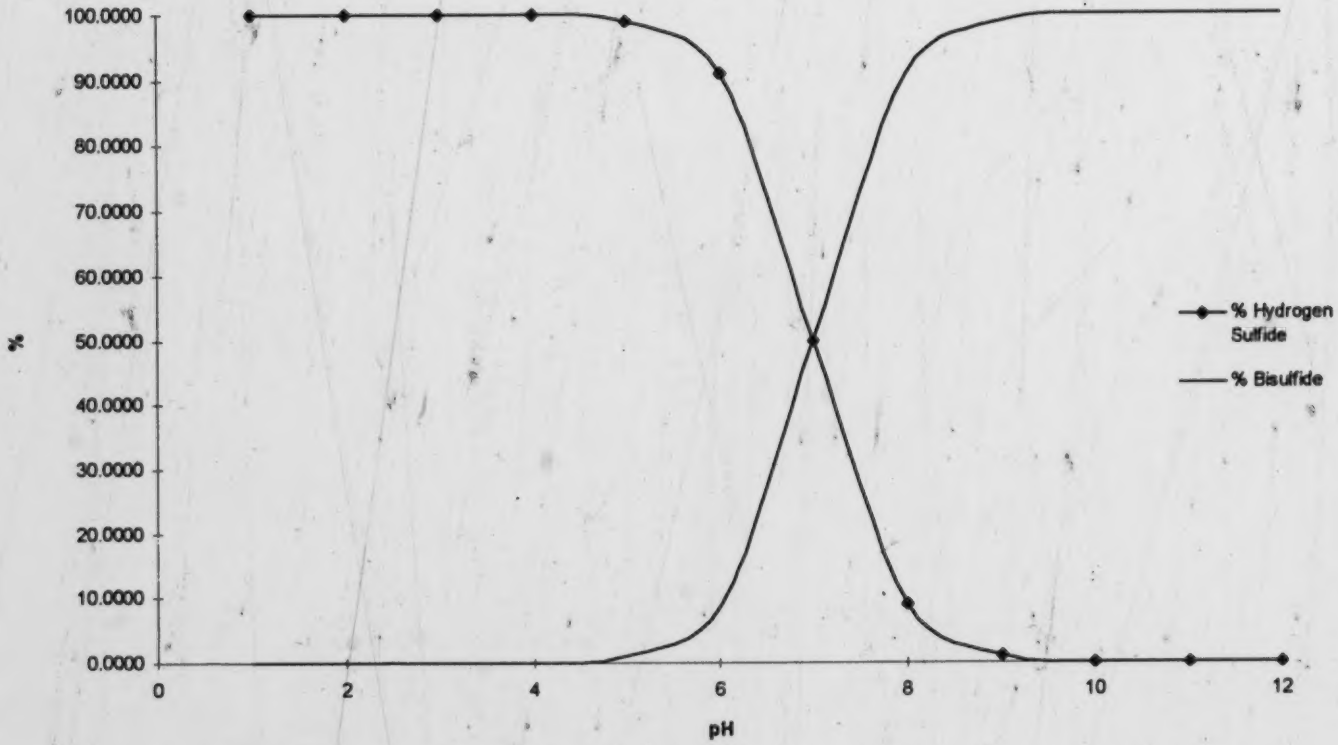

Figure 9. % Hydrogen Sulfide and Bisulfide Versus pH.

Table 14. pH Adjustment of Digester Sludge

Impinger NaOH Conc. (N)	Sludge pH	Total Sulfide (per half litre of sludge)
0.5	7.25	8.065
0.5	7.25	7.039
1	2.31	17.28
1	2.31	17.07
2	2.31	23.97
2	2.31	19.27

To determine the proportion of the sulfide that exists in the solid form, the sludge was centrifuged to separate the solid and the liquid portion of the sludge. Tests were then conducted on the solid portion which was diluted with de-ionized water. Initially, no S^{2-}, HS^- or H_2S should be present in the liquid portion of the diluted sample. Acid was added to the solution to bring the pH to slightly above 2. Results showed that 16.85 mg (per half litre of sludge) of sulfide was present, signifying that the acid most likely dissolved some solid sulfide compounds (such as metal sulfides). Another test was conducted on the solid portion of the sludge (again diluted with de-ionized water). This time no HCl was added, and no sulfide was detected in the diluted sample. This indicates that adding acid does change the solubility of certain solids in the sludge.

A ferrous sulfide precipitate will form when $FeCl_2$, $FeCl_3$ or $FeCl_2$ waste solution is added to sludge. This reduces the amount of hydrogen sulfide in the liquid portion of the sludge. In addition to shifting the equilibrium of aqueous species shown in equations 24 and 25 to favor H_2S formation, the subsequent addition of acid will also dissolve the ferrous sulfide precipitate. This leads to a misrepresentation in the amount of hydrogen

sulfide removed. Calculations show that lowering the pH below 3 increases the solubility of the ferrous sulfide precipitate. As a result, the ferrous sulfide dissociates, leading to skewed results. To confirm the calculations, 280 mg of a $FeCl_2 \bullet 4H_20$ solution was added to a 40 mg/L sulfide solution. The solution immediately turned black, indicating the formation of FeS. When the pH was adjusted to slightly above 2 the solution immediately turned clear again, signifying that the ferrous sulfide precipitate that originally formed dissociated and dissolved into the solution. Therefore, the addition of acid was discontinued to prevent any of the above problems from occurring.

The Gold Bar wastewater treatment plant digesters operate within a pH range of 7.1 to 7.3. All further experiments were conducted as close as possible to this pH range.

4.1.2 Helium Flow Rate

An inert gas, such as helium, is utilized since it does not react with any of the digester gases. To purge (similar to sparging and stripping) the greatest amount of hydrogen sulfide in the shortest amount of time, a sufficiently high gas flow rate is required. Although the high flow rate must not cause any loss of NaOH from the impinger. The helium flow through each reactor (measured downstream of each impinger to take into consideration headlosses) was maintained at 1.2 L/min. This is equivalent to a flowmeter reading of 45, as shown in Figure 10. A rotameter type flowmeter was used throughout the experiments. The flowmeter was calibrated using a Wet Test meter (GCA/Precision Scientific), where each flowmeter reading correlated with a specific flowrate. The helium flow through each of the four reactors was maintained at 1.2 L/min, by checking periodically with the flowmeter and adjusting as required.

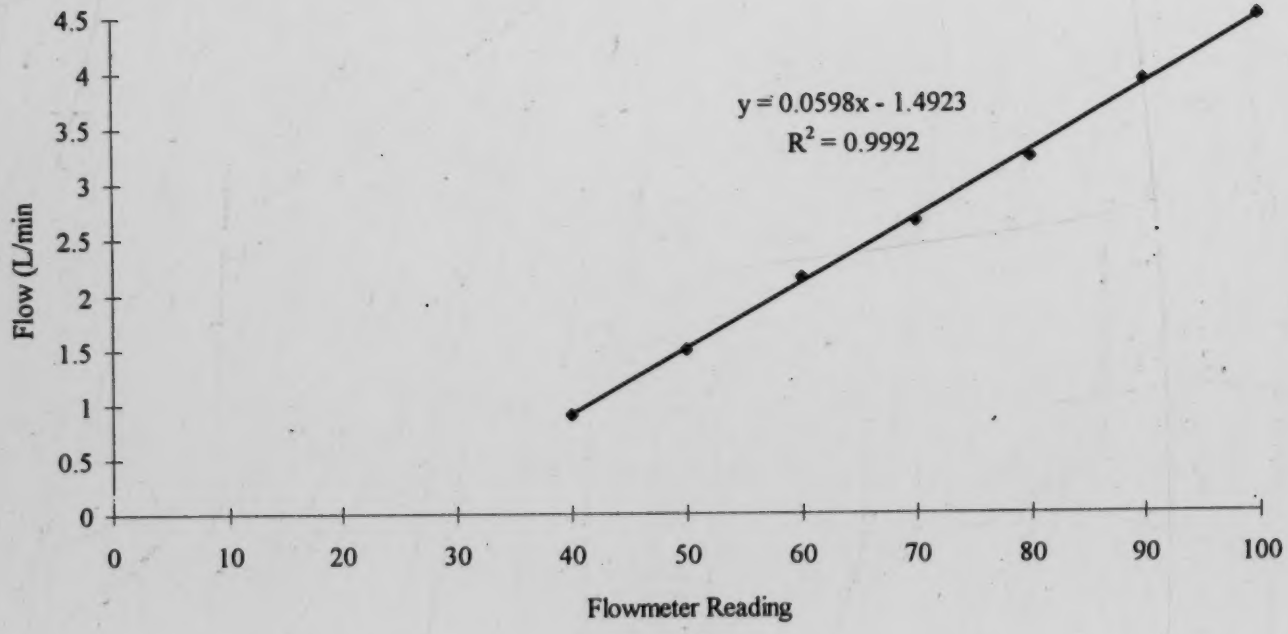

Figure 10. Calibration Curve For Flowmeter.

4.1.3 Buffering Sludge

When gas stripping is performed in solutions which have CO_2 gas, such as in digester sludge, removal of the CO_2 will result in an increase in the pH of the solution. This suggests that when the digester sludge is stripped of hydrogen sulfide and other gases (including CO_2), the pH will increase with time resulting in less hydrogen sulfide being removed (see Figure 9).

As shown in Table 15, the pH of the sludge increases as the sludge is sparged with helium. To simulate the digester pH at the Gold Bar Wastewater Treatment Plant, the pH of the sludge must be prevented from increasing during purging. To prevent a change in pH, a phosphate buffer was added to the sludge. 120 mL of a 0.4M phosphate buffer prevented a large change in the pH. Although the pH of the sludge still increased to approximately 7.55 after 30 minutes of sparging, such a pH still allowed a large amount of hydrogen sulfide to be removed.

Table 15. Change in pH of Sludge with Continual Purging

Time (min)	pH of sludge before stripping	pH of sludge after stripping
30	7.33	8.10
30	7.31	8.12
60	7.28	8.42
60	7.31	8.40
30 (with buffer)	7.30	7.55

4.1.4 Scrubber Solution

A sodium hydroxide solution was used to capture any hydrogen sulfide which was purged out of the digester sludge. When the digester gas is bubbled through the sodium

hydroxide solution, any hydrogen sulfide gas present in the gas stream is instantaneously converted to sulfide ions.

A conservative sodium hydroxide concentration of 2N was used in these experiments. The capacity to capture the hydrogen sulfide is a function of the concentration of the NaOH. The higher the concentration, the greater the capacity to remove hydrogen sulfide. Concentrations below 0.4N were unable to capture all of the hydrogen sulfide stripped out of the digester sludge (untreated samples). The inability to trap all of the hydrogen sulfide is due to the NaOH being neutralized by the hydrogen sulfide gases being bubbled through the NaOH solution. A noticeable drop in the pH of the NaOH was observed when the concentration was below 0.4N. To remove all of the hydrogen sulfide out of the gas stream, the pH must be maintained at approximately 12.6 without any substantial drop.

As shown in Table 16, three impingers were placed in series in order to find the NaOH concentration required for all the hydrogen sulfide gas to be captured in the first impinger. These tests indicate that a 0.4N NaOH concentration is adequate to capture 7 mg of sulfide from 0.5 litres of sludge. Therefore, only one impinger with a sufficiently high NaOH concentration was used in further experiments to capture all of the sulfide.

A Mettler Toledo model DL53 automatic titrator, along with a Mettler silver tip electrode (model DM 141-SC) were used throughout the experiments to quantify the amount of sulfide captured in the NaOH solution. Tests were performed to ensure that varying the concentration of the NaOH did not inhibit the ability of the automatic titrator's

electrode to quantify the amount of sulfide in the NaOH solution. Test results are shown in Table 17.

Table 16. Concentration of Sulfide in Impinger Versus Different NaOH Concentrations

		<---------- 3 Impingers in Series ---------->		
Conc. of NaOH (Normality)	Time (min)	S^{2-} Conc. 1st. Impinger (mg)	S^{2-} Conc. 2nd Impinger (mg)	S^{2-} Conc. 3rd Impinger (mg)
0.2	30	5.844	1.519	-
0.2	30	5.156	1.730	0.350
0.4	30	7	0	0

Table 17. Sulfide Titrated Versus Varying NaOH Concentrations

Titrator Cup	NaOH Conc. (Normality)	S^{2-} Added (mg)	S^{2-} Titrated (mg)
1	0	6	5.708
2	0.15	6	5.821
3	0.3	6	5.674
4	0.8	6	5.524
5	1.2	6	5.628
6	1.5	6	5.820

6 mg of sulfide was added to each titrator cup, where each had different concentrations of NaOH. As shown in Table 17, the varying concentrations of NaOH results in approximately similar amounts of sulfide being measured. This indicates that there is no relationship between the NaOH concentration and the electrode's ability to quantify the available sulfide.

4.1.5 Diffuser Type

A spherical stone diffuser was used to disperse the helium gas through the sludge. Fine bubbles were emitted, providing a higher degree of purging compared to that which is provided by coarse bubble diffusers. Therefore, the spherical stone fine bubble diffuser

provides an efficient mass transfer rate of hydrogen sulfide from the liquid phase to the gas phase.

4.1.6 Calibration of Mixer Settings

A total of four Corning magnetic stirrers were used throughout the experiments. Mixing speed was maintained at the maximum speed possible to ensure sufficient dispersion of the chemical added. The maximum rotations per minute applied to the sludge reactor was approximately 200 rpm. This speed provided sufficient mixing and prevented any erratic movement of the magnetic stir bar (9.5mm diameter and 51mm in length).

Due to each magnetic stirrer being different, each mixer had to be calibrated. Calibration of each mixer was carried out with a digital tachometer by Shimpo (DT-201). The rotations per minute of the stir bar was measured in an empty reactor bottle. The required settings for each mixer (to provide 200 rpm) were obtained with the digital tachometer.

4.1.7 Calibration of Automatic Titrator

A Mettler Toledo model DL53 automatic titrator, along with a Mettler silver tip electrode (model DM 141-SC) were used throughout the experiments. These instruments quantified the amount of sulfide captured in the NaOH solution from the sludge. Automatic titrator input values are shown in Appendix G. To ensure the validity of the results generated by the titrator, a solution of sodium sulfide was used to calibrate the instrument. A known amount of sulfide was placed in the titrator cup and then titrated with the 0.05N silver nitrate titrant. When the results generated by the automatic titrator

were close (± 6%) to the known theoretical amount of sulfide added, this would suggest that the instrument was properly calibrated. Though a slight difference between the theoretical amount of sulfide added and the amount titrated is expected, since a small amount of the sulfide will be oxidized by the oxygen in the water.

The amount of sulfide available was identified by the determination of the equivalence point. The equivalence point is defined as the point at which a sufficient amount of titrant ($AgNO_3$) has been added to react with the analyte (sulfide). At this point just enough $AgNO_3$ has been added to complete the reaction (Atkins, 1989). A typical titration curve is shown in Figure 11.

4.1.8 Sludge Sampling

At the Gold Bar Wastewater Treatment Plant there are a total of six high rate anaerobic digesters. Digesters 1 to 4 have a standard type of mixing mechanism, including recirculation of biogas and heat exchangers. Digesters 5 and 6 also have heat exchangers, although the recirculation of biogas is provided by cannon mixers allowing better mixing and less stratification (compared to digesters 1 to 4). Sludge was sampled from digesters 3 and 6.

Sludge was sampled from 2 different levels at the sludge sampling ports. First samples were taken from the 7.9 m level, representing a continuously mixed sample of sludge from the mid-height level of the 15.8 m digester. The second sample was taken

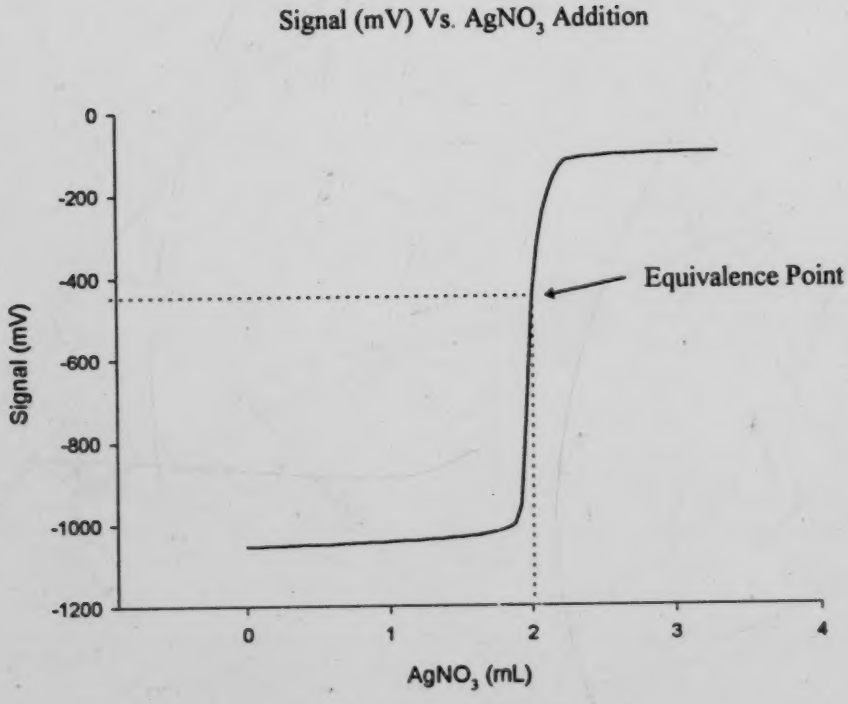

Figure 11. Typical Titration Curve.

from the cone section, which is the bottom of the digester. This sample represented sludge that would be conveyed and stored in the Clover Bar lagoons. Both sampling locations are shown in Figure 6.

For the experiments performed on the 7.9 m sludge samples, collection of the sample could be done at any time required. For the sludge samples from the cone section, samples could only be collected when the digester was being pumped down. Collection of the sludge at any other time, would not give a representative sample. Since the sampling port for the cone section was at a higher level than the actual cone section, settling of the sludge would occur in the pipe connecting the sampling port and the actual cone section.

Samples from the 7.9 m and cone levels were collected into 1 litre glass reactor bottles. Though the collection procedure for each level was different due to the limitations described in the previous paragraph. For samples collected at the 7.9 m level, eight glass 1 litre reactors would be filled with half a litre of sludge each and then plugged with a pre-made stopper (fitted with leur lok valve and glass tubings). The pre-made stopper would prevent the loss of any gases volatilizing out of the digester sludge. The samples would then immediately be brought to the laboratory on site to be analyzed for sulfide content. Four samples of sludge were tested per run. When these analyses were completed, more samples could be collected from the sampling port and associated experiments performed.

For the experiments performed on the cone section of the sludge, the volume of sludge required for an entire day of tests would need to be collected when the digester was being pumped down (which occurs 2 to 3 times a day). Usually 12, 1 litre reactor

bottles would be filled completely and stoppered, leaving a small headspace at the top of the reactor. Although the headspace allowed a small loss of digester gas, it would confine the gas pressure in the reactor to the neck. This would prevent the possible explosion of the glass reactor bottle as well as minimize the chance of the stopper exploding off the bottle. The sludge would then be brought to the laboratory on site, and experiments would be performed on the sludge as required. The same experimental procedure was performed on sludge samples from the two different levels. See Appendix G for the experimental procedure.

4.2 Chemical Preparation and Additions

4.2.1 Ferrous Chloride and Ferric Chloride Solutions

Throughout the experiments either a 5 g/L stock solution of ferrous chloride ($FeCl_2 \bullet 4H_20$) or a 10 g/L stock solution of ferric chloride ($FeCl_3 \bullet 6H_20$) were utilized. Both of the chemicals were of reagent grade, purchased from Fisher Scientific Co., Edmonton, Alberta. Preparation of each chemical is outlined in Appendix G.

4.2.2 Ferrous Chloride Waste Solution

A waste product of ferrous chloride was generously provided by DAAM Galvanizing Inc., Edmonton, Alberta. It was tested to determine whether a waste product would provide a substantial decrease in the amount of hydrogen sulfide available in the digester sludge. As well, testing such a product would show the relative performance to the other chemicals used: ferrous and ferric chloride. Table 18 shows the characteristics of the waste product. As shown a variety of different metals exist in the waste product,

Table 18. Characteristics of Ferrous Chloride Waste Solution

Element	mg/L
Aluminum	68.6
Antimony	5.28
Arsenic	<0.25
Barium	10.6
Beryllium	<0.0125
Bismuth	6.04
Boron	<0.050
Cadmium	0.43
Calcium	216
Chromium	134
Cobalt	11.5
Copper	223
Iron	153000
Lead	141
Lithium	0.549
Manganese	2100
Magnesium	8.36
Molybdenum	24.1
Nickel	153
Phosphorus	227
Potassium	206
Selenium	40.4
Silicon	9.22
Silver	0.483
Strontium	1.7
Sodium	2320
Sulfur	84.7
Titanium	15.9
Thallium	2.01
Tin	8.31
Vanadium	11.3
Zinc	9630

*32 element scan performed by
Norwest Labs, Edmonton, Canada.

where the iron and zinc concentrations are the highest. A stock solution was prepared by diluting the waste solution 1:100 with de-ionized water (see Appendix G).

4.2.3 Ferrous and Ferric Chloride Additions

With the addition of ferrous chloride or ferric chloride to the anaerobic sludge, insoluble ferrous or ferric compounds form. As outlined previously in section 3.4.1.3, reactions between ferrous salts and dissolved sulfides form a FeS precipitate as shown,

$$Fe^{2+} + HS^- \Longleftrightarrow FeS + H^+ \qquad (27)$$

Theoretically ferric salts react in a similar manner when in the presence of dissolved sulfides,

$$2Fe^{3+} + 3HS^- \Longleftrightarrow Fe_2S_3 + 3H^+ \qquad (28)$$

leading to the formation of a ferric sulfide precipitate. Because the solubility of ferric hydroxide ($Fe(OH)_3$) is lower than that of ferric sulfide (Fe_2S_3), the $Fe(OH)_3$ precipitate will form before the Fe_2S_3 precipitate. However, in the presence of sulfides (a strong reducing ion) and other reducing material in the sludge, the ferric ions are reduced to ferrous ions. This will result in the formation of a ferrous sulfide precipitate and a reduction in the amount of hydrogen sulfide available.

The addition of the ferrous waste solution will also allow the formation of a ferrous sulfide precipitate. Since there are a variety of other metals available in the waste product, other metal precipitates such as zinc sulfide will also form.

Appropriate dosages of each chemical were added to each sludge sample to yield percent reductions of sulfide between 50 and 90 percent. Typical dosages are shown in Table 19. These dosages provided a relationship between the amount of chemical added and the reduction of sulfide.

Table 19. Dosage Range Added of Each Chemical

Chemical	Average dosage range as Fe^{2+} or Fe^{3+} (mg/L)
$FeCl_2$	0 to 60.0
$FeCl_3$	0 to 330
$FeCl_2$ Waste Solution	0 to 55

4.3 Experimental Design

Sulfide levels in anaerobic digesters naturally change depending on the amount of runoff experienced in the catchment area. When a high amount of runoff occurs, there is a significant dilution of the sanitary waste. This leads to a decrease in the sulfide levels in the anaerobic digesters. Likewise when there is very little runoff, such as in the winter, the sulfide levels are very high in the digester. Therefore, depending on the weather, low, moderate or high sulfide levels will exist. Experiments were conducted to find the amount of chemical (either ferrous chloride, ferric chloride and ferrous chloride waste solution) required to attain certain percent reductions in the amount of sulfide available in the digester when sulfide levels were low, moderate and high. A low sulfide level range is between 1.5 and 3.5 mg, a moderate sulfide level range between 3.5 and 6 mg and a high sulfide level range is 6 mg and above.

Each experimental run consisted of 4 reactors containing 0.5L of sludge each, as shown in Figure 8. Tables 20 to 31 show the experimental arrangements for each stage of the study.

4.3.1 Statistics

To ensure that each result attained was statistically sound, replicates were performed. Each experiment (dose added) was repeated four times. A mean and standard

deviation were calculated for each experimental run. As well, a 95% confidence interval or maximum error of estimate (E) for each mean was calculated using (Miller *et al.*, 1990)

$$E = \frac{t_{\alpha} \bullet s}{n^{0.5}} \qquad (29)$$

A 95% confidence interval ensures that 95 % of the time, the sample mean will be within the calculated interval. The approximate average percent error for each mean was ± 6.2 percent. Examples of all of the above statistics are shown in Table 32. Variations in each of the results are due to the inconsistency of the sludge samples. Although samples are taken from the same sampling ports, no two sludge samples are exactly the same. See Appendix A and B for the statistical values of all the tests.

Table 20. Experimental Arrangement for Stage 1 Study, Digester 3

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_2$ Waste Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	7.9	30	0	1.2	200	120	2
2	Low	7.9	30	2	1.2	200	120	2
3	Low	7.9	30	5	1.2	200	120	2
4	Low	7.9	30	10	1.2	200	120	2
5	Low	7.9	30	15	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_3$ $6H_20$ (10g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	7.9	30	0	1.2	200	120	2
2	Low	7.9	30	50	1.2	200	120	2
3	Low	7.9	30	75	1.2	200	120	2
4	Low	7.9	30	100	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_2$ $4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	7.9	30	0	1.2	200	120	2
2	Low	7.9	30	30	1.2	200	120	2
3	Low	7.9	30	50	1.2	200	120	2
4	Low	7.9	30	75	1.2	200	120	2
5	Low	7.9	30	120	1.2	200	120	2

Table 21. Experimental Arrangement for Stage 2 Study, Digester 3

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_2$ Waste Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Moderate	7.9	30	0	1.2	200	120	2
2	Moderate	7.9	30	4	1.2	200	120	2
3	Moderate	7.9	30	7	1.2	200	120	2
4	Moderate	7.9	30	12	1.2	200	120	2
5	Moderate	7.9	30	17	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_3$ $6H_20$ (10g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Moderate	7.9	30	0	1.2	200	120	2
2	Moderate	7.9	30	20	1.2	200	120	2
3	Moderate	7.9	30	35	1.2	200	120	2
4	Moderate	7.9	30	50	1.2	200	120	2
5	Moderate	7.9	30	65	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_2$ $4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Moderate	7.9	30	0	1.2	200	120	2
2	Moderate	7.9	30	5	1.2	200	120	2
3	Moderate	7.9	30	8	1.2	200	120	2
4	Moderate	7.9	30	12	1.2	200	120	2
5	Moderate	7.9	30	18	1.2	200	120	2

Table 22. Experimental Arrangement for Stage 3 Study, Digester 3

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_2$ $4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	High	7.9	30	0	1.2	200	120	2
2	High	7.9	30	6.2	1.2	200	120	2
3	High	7.9	30	9.9	1.2	200	120	2
4	High	7.9	30	15	1.2	200	120	2
5	High	7.9	30	24.8	1.2	200	120	2

Table 23. Experimental Arrangement for Stage 4 Study, Digester 3

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2$ Waste Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	Cone	30	0	1.2	200	120	2
2	Low	Cone	30	5	1.2	200	120	2
3	Low	Cone	30	7.5	1.2	200	120	2
4	Low	Cone	30	10	1.2	200	120	2
5	Low	Cone	30	15	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_3$ $6H_20$ (10g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	Cone	30	0	1.2	200	120	2
2	Low	Cone	30	15	1.2	200	120	2
3	Low	Cone	30	30	1.2	200	120	2
4	Low	Cone	30	50	1.2	200	120	2
5	Low	Cone	30	80	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2$ $4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	Cone	30	0	1.2	200	120	2
2	Low	Cone	30	6	1.2	200	120	2
3	Low	Cone	30	10	1.2	200	120	2
4	Low	Cone	30	13	1.2	200	120	2
5	Low	Cone	30	20	1.2	200	120	2

Table 24. Experimental Arrangement for Stage 5 Study, Digester 3

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2$ Waste Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Moderate	Cone	30	0	1.2	200	120	2
2	Moderate	Cone	30	3.5	1.2	200	120	2
3	Moderate	Cone	30	6	1.2	200	120	2
4	Moderate	Cone	30	8	1.2	200	120	2
5	Moderate	Cone	30	13	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_3 6H_20$ (10g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Moderate	Cone	30	0	1.2	200	120	2
2	Moderate	Cone	30	12	1.2	200	120	2
3	Moderate	Cone	30	25	1.2	200	120	2
4	Moderate	Cone	30	40	1.2	200	120	2
5	Moderate	Cone	30	70	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2 4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Moderate	Cone	30	0	1.2	200	120	2
2	Moderate	Cone	30	4	1.2	200	120	2
3	Moderate	Cone	30	7	1.2	200	120	2
4	Moderate	Cone	30	11	1.2	200	120	2
5	Moderate	Cone	30	16	1.2	200	120	2

Table 25. Experimental Arrangement for Stage 6 Study, Digester 3

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2$ Waste Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	High	Cone	30	0	1.2	200	120	2
2	High	Cone	30	6	1.2	200	120	2
3	High	Cone	30	8	1.2	200	120	2
4	High	Cone	30	12	1.2	200	120	2
5	High	Cone	30	20	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2$ $4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	High	Cone	30	0	1.2	200	120	2
2	High	Cone	30	7	1.2	200	120	2
3	High	Cone	30	9	1.2	200	120	2
4	High	Cone	30	13	1.2	200	120	2
5	High	Cone	30	20	1.2	200	120	2

Table 26. Experimental Arrangement for Stage 7 Study, Digester 6

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_2$ Waste Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	7.9	30	0	1.2	200	120	2
2	Low	7.9	30	5	1.2	200	120	2
3	Low	7.9	30	7.5	1.2	200	120	2
4	Low	7.9	30	10	1.2	200	120	2
5	Low	7.9	30	15	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_3$ $6H_20$ (10g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	7.9	30	0	1.2	200	120	2
2	Low	7.9	30	15	1.2	200	120	2
3	Low	7.9	30	30	1.2	200	120	2
4	Low	7.9	30	50	1.2	200	120	2
5	Low	7.9	30	80	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_2$ $4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	7.9	30	0	1.2	200	120	2
2	Low	7.9	30	3	1.2	200	120	2
3	Low	7.9	30	6	1.2	200	120	2
4	Low	7.9	30	10	1.2	200	120	2
5	Low	7.9	30	13	1.2	200	120	2

Table 27. Experimental Arrangement for Stage 8 Study, Digester 6

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_2$ Waste Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Moderate	7.9	30	0	1.2	200	120	2
2	Moderate	7.9	30	6	1 2	200	120	2
3	Moderate	7.9	30	8	1.2	200	120	2
4	Moderate	7.9	30	13	1 2	200	120	2
5	Moderate	7.9	30	20	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_3$ $6H_20$ (10g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Moderate	7.9	30	0	1.2	200	120	2
2	Moderate	7.9	30	12	1 2	200	120	2
3	Moderate	7.9	30	25	1 2	200	120	2
4	Moderate	7.9	30	40	1.2	200	120	2
5	Moderate	7.9	30	60	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_2$ $4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Moderate	7.9	30	0	1.2	200	120	2
2	Moderate	7.9	30	6	1 2	200	120	2
3	Moderate	7.9	30	10	1 2	200	120	2
4	Moderate	7.9	30	13	1 2	200	120	2
5	Moderate	7.9	30	20	1 2	200	120	2

Table 28. Experimental Arrangement for Stage 9 Study, Digester 6

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_2$ Waste Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	High	7.9	30	0	1.2	200	120	2
2	High	7.9	30	7	1.2	200	120	2
3	High	7.9	30	10	1.2	200	120	2
4	High	7.9	30	14	1.2	200	120	2
5	High	7.9	30	20	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_3$ $6H_20$ (10g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	High	7.9	30	0	1.2	200	120	2
2	High	7.9	30	12	1.2	200	120	2
3	High	7.9	30	25	1.2	200	120	2
4	High	7.9	30	40	1.2	200	120	2
5	High	7.9	30	70	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level (m)	Sparge Duration (min)	$FeCl_2$ $4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	High	7.9	30	0	1.2	200	120	2
2	High	7.9	30	4	1.2	200	120	2
3	High	7.9	30	7	1.2	200	120	2
4	High	7.9	30	11	1.2	200	120	2
5	High	7.9	30	18	1.2	200	120	2

Table 29. Experimental Arrangement for Stage 10 Study, Digester 6

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2$ Waste Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	Cone	30	0	1.2	200	120	2
2	Low	Cone	30	5	1.2	200	120	2
3	Low	Cone	30	7.5	1.2	200	120	2
4	Low	Cone	30	10	1.2	200	120	2
5	Low	Cone	30	15	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_3$ $6H_20$ (10g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	Cone	30	0	1.2	200	120	2
2	Low	Cone	30	20	1.2	200	120	2
3	Low	Cone	30	35	1.2	200	120	2
4	Low	Cone	30	50	1.2	200	120	2
5	Low	Cone	30	80	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2$ $4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Low	Cone	30	0	1.2	200	120	2
2	Low	Cone	30	6	1.2	200	120	2
3	Low	Cone	30	10	1.2	200	120	2
4	Low	Cone	30	13	1.2	200	120	2
5	Low	Cone	30	20	1.2	200	120	2

Table 30. Experimental Arrangement for Stage 11 Study, Digester 6

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2$ Waste Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Moderate	Cone	30	0	1.2	200	120	2
2	Moderate	Cone	30	4	1.2	200	120	2
3	Moderate	Cone	30	8	1.2	200	120	2
4	Moderate	Cone	30	12	1.2	200	120	2
5	Moderate	Cone	30	17	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2\ 4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	Moderate	Cone	30	0	1.2	200	120	2
2	Moderate	Cone	30	20	1.2	200	120	2
3	Moderate	Cone	30	35	1.2	200	120	2
4	Moderate	Cone	30	55	1.2	200	120	2
5	Moderate	Cone	30	80	1.2	200	120	2

Table 31. Experimental Arrangement for Stage 12 Study, Digester 6

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2$ Waste Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	High	Cone	30	0	1.2	200	120	2
2	High	Cone	30	7	1.2	200	120	2
3	High	Cone	30	10	1.2	200	120	2
4	High	Cone	30	14	1.2	200	120	2
5	High	Cone	30	20	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_3$ $6H_20$ (10g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	High	Cone	30	0	1.2	200	120	2
2	High	Cone	30	12	1.2	200	120	2
3	High	Cone	30	25	1.2	200	120	2
4	High	Cone	30	40	1.2	200	120	2
5	High	Cone	30	70	1.2	200	120	2

Run	Sulfide Level in Digester	Digester Sampling Level	Sparge Duration (min)	$FeCl_2$ $4H_20$ (5g/L) Dose (mL)	Helium Flow Rate (L/min.)	Mixing Speed (rpm)	0.4M Phosphate Buffer (mL)	NaOH Conc. (Normality)
1	High	Cone	30	0	1.2	200	120	2
2	High	Cone	30	30	1.2	200	120	2
3	High	Cone	30	40	1.2	200	120	2
4	High	Cone	30	60	1.2	200	120	2
5	High	Cone	30	90	1.2	200	120	2

Table 32. Statistics For a Set of Experiments on Digester Sludge

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ $4H_2O$ 5g/L (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg)	Mean (mg)	Standard Deviation	Error for 95% confidence	Average % Reduction	% Error Percent Reduction (+ or -)
30	120	0	0.0	4.31					
30	120	0	0.0	4.07					
30	120	0	0.0	4.77					
30	120	0	0.0	4.61	4.44	0.310	0.493	0.0	11.1
30	120	5	14.0	1.59					
30	120	5	14.0	1.72					
30	120	5	14.0	1.57					
30	120	5	14.0	1.97	1.71	0.184	0.293	61.5	6.6
30	120	8	22.5	0.87					
30	120	8	22.5	1.33					
30	120	8	22.5	1.08					
30	120	8	22.5	1.11	1.10	0.187	0.297	75.3	6.7
30	120	12	33.7	0.75					
30	120	12	33.7	0.88					
30	120	12	33.7	0.68					
30	120	12	33.7	0.73	0.76	0.09	0.14	82.9	3.1
30	120	18	50.6	0.64					
30	120	18	50.6	0.69					
30	120	18	50.6	0.81					
30	120	18	50.6	0.76	0.73	0.07	0.12	83.6	2.7

4.4 Removal of Hydrogen Sulfide

4.4.1 Hydrogen Sulfide Stripping

The removal of hydrogen sulfide was achieved by purging with helium. The hydrogen sulfide in the anaerobic sludge exists in two phases, the liquid and gas phase. Removal of the hydrogen sulfide in the liquid phase is governed by Fick's Law. The rate of mass transfer of the hydrogen sulfide from the liquid phase to the gas phase is described by the flux. The rate of flux is a function of the driving force and is a mass transfer of material per time through a unit area. The driving force being the concentration difference between the bulk liquid and the liquid film interface. Considering a steady state mass transfer model, the rate at which the gas reaches the interface from the liquid phase must equal the rate at which the gas leaves the interface and enters the gas phase (AWWA, 1990). A representation of the two film theory is shown in Figure 12. In both the liquid and gas phases, the flux relationship can be described by Fick's Law (AWWA, 1990):

$$F = \frac{dW}{dt\ A} = k_G(p_G - p_I) = k_L(c_I - c_L) \qquad (30)$$

F = Flux

W = mass transferred

A = Area

t = Time

c = mass concentration of liquid phase, where subscript L denotes bulk concentration and subscript I interface concentration

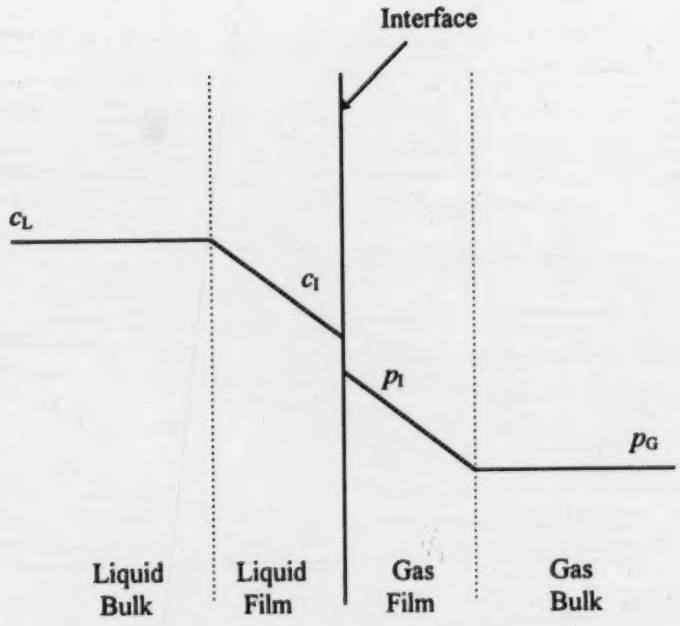

Figure 12. Two Film Theory (AWWA, 1990).

p = gas phase concentration, where subscript G denotes bulk concentration and subscript I denotes interface concentration

k = interface mass transfer coefficient

Turbulence and mixing can increase the mass transfer of gas through the liquid by reducing the thickness of the liquid film, which increases the transfer coefficient k_L. Thus, adequate turbulence and mixing should be provided, to strip out the maximum amount of hydrogen sulfide in the least amount of time.

Throughout the experiments, a sufficient amount of helium and mixing was provided to the sludge in each of the reactors. This allowed a maximum amount of hydrogen sulfide to be stripped out of the sludge. 30 minutes was the time designated for each experiment. Thorough experiments have shown that 30 minutes was an optimum time, considering the amount of hydrogen sulfide to be removed and a practical time limit for each run.

Spiking the sludge with a known amount of sulfide, allowed two points to be confirmed. First, that the material being quantified by the automatic titrator was sulfide. Second, that a majority of the hydrogen sulfide available in the liquid was being stripped out of the solution in 30 minutes. To confirm the above, two sludge samples were spiked with 4 mg of sulfide. Depending on the amount recovered of the 4 mg added, a percent recovery of the sulfide originally present in the sludge was determined.

Two control samples of sludge were exposed to the same conditions as in Table 33 (except for sulfide additions). The average amount of sulfide titrated was 6.76 mg (without sulfide spiking) . With the addition of 4 mg of sulfide to the sludge, the average

Table 33. Sulfide Recovered out of Spiked Sludge Sample

Time (min)	NaOH Conc. (N)	pH of sludge before stripping (with buffer)	pH of sludge after stripping	Amount of Phosphate Buffer (mL) pH = 6.74	S^{2-} added to sludge (mg)	S^{2-} Conc. (mg)
30	2	6.92	7.55	90	4	10.54
30	2	6.92	7.52	90	4	10.70
					Average	= 10.62

amount of sulfide titrated was 10.62mg (as shown in Table 33). Therefore,

10.62mg - 6.76mg = 3.86mg of sulfide recovered

$$\%\,Recovery\ of\ sulfide = \frac{4mg - 3.86mg}{4mg} \times 100 = 96.5\%$$

This experiment proved that the material quantified by the titration procedure was actually sulfide. As well, a majority (96.5%) of the hydrogen sulfide present in the liquid portion of the sludge was being stripped in the 30 minutes allotted for each run.

4.4.2 Diffusion and Desorption

Hydrogen sulfide also exists in the liquid portion of the micro and macro pores of the solid sludge matrix. Diffusion of the hydrogen sulfide from the pores occurs when a concentration gradient exists between the liquid in the pores (floc liquid) and the liquid surrounding the solid sludge matrix (bulk liquid). Such a gradient develops when the hydrogen sulfide in the bulk liquid is purged with helium. The hydrogen sulfide then diffuses out of the floc liquid and into the bulk liquid, where the diffused hydrogen sulfide is purged once again.

Desorption from the solid material, within the floc, will occur when the hydrogen sulfide has diffused out of the interstitial pores. Again this is due to a concentration

gradient between the hydrogen sulfide in the solid material and the liquid in the micro and macro pores. Thus any sulfide that will desorb into the pores, will then diffuse out of the pores and be stripped out of solution. A schematic representation of the sludge floc matrix is shown in Figure 13.

4.4.3 Biological Production

Another source of hydrogen sulfide is from the constant biological activity in the sludge. Sulfate reducing bacteria thrive in the anaerobic sludge and reduce available sulfate to sulfide. However, the reduction process is slow and can be considered to be negligible since the duration of most of the tests was 30 minutes in length.

4.4.4 Hydrogen Sulfide Recovery Versus Time

Developing a relationship for the recovery of hydrogen sulfide with time encompasses all of the above: diffusion, desorption and biological production. The recovery of the hydrogen sulfide from the sludge can be explained in two stages, as shown in Figure 14. The highest rate of removal occurs in the first stage. Here the major source of hydrogen sulfide is from the liquid portion of the sludge. As more of the hydrogen sulfide is removed from the liquid, a diffusion of the hydrogen sulfide out of the interstitial pores begins to occur. As well, a concentration gradient develops between the liquid portion in the interstitial pores and the solid material, resulting in desorption. Biological production of hydrogen sulfide is another source, though negligible.

In stage 2, a linear relationship exists between the recovery of hydrogen sulfide and time. The linear relationship signifies that the recovery of hydrogen sulfide is limited, and that the liquid portion of the sludge is no longer the major source of the hydrogen sulfide.

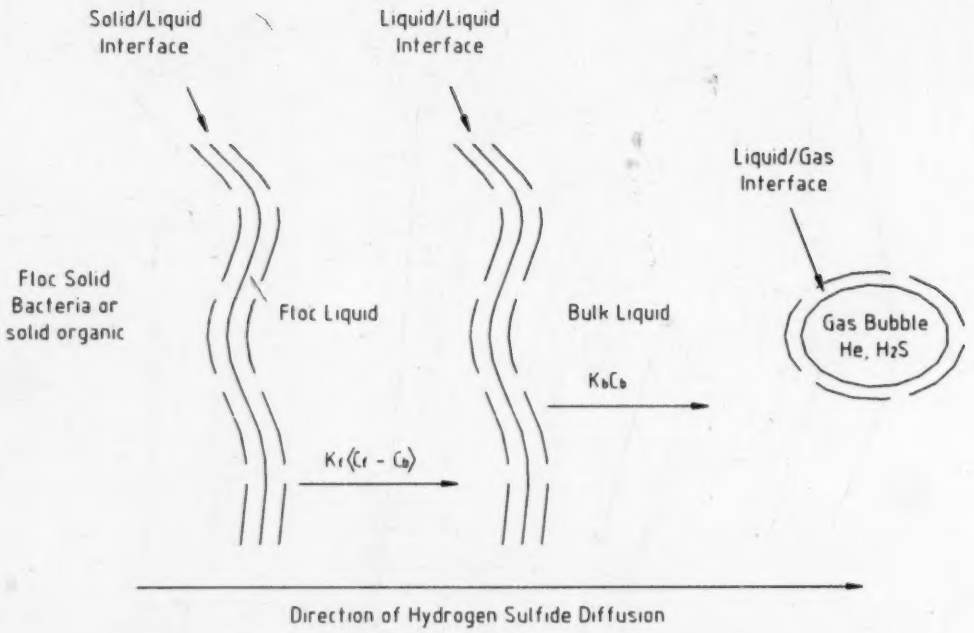

Figure 13. Schematic Representation of the Sludge Floc Matrix.

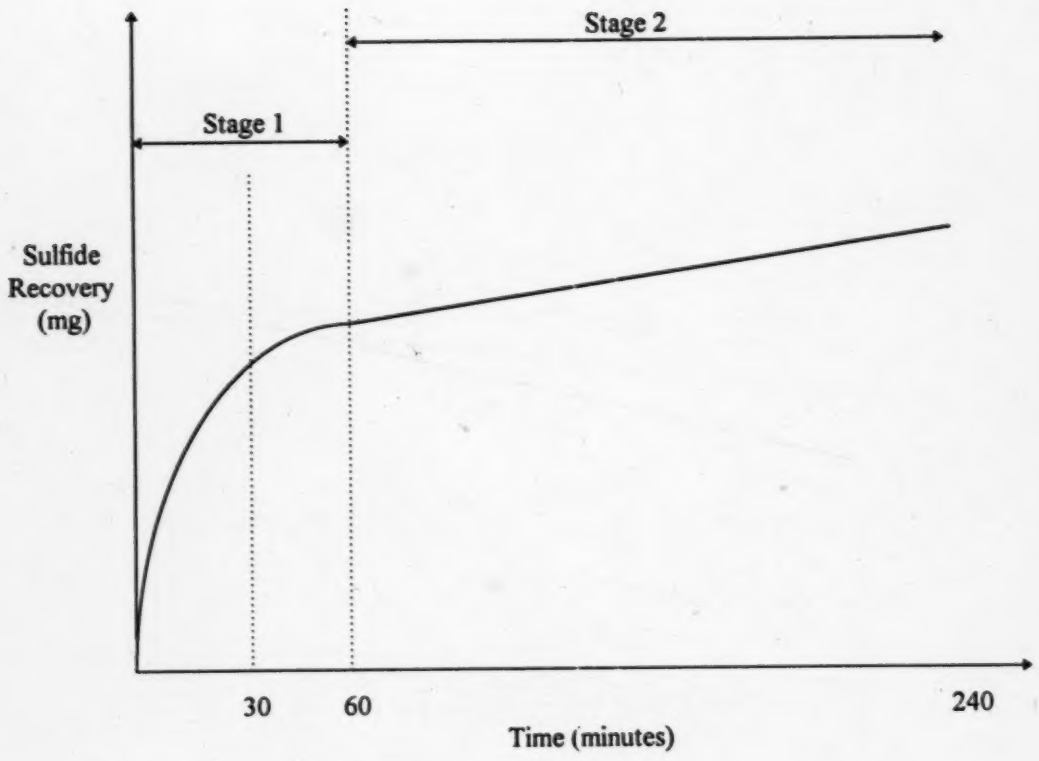

Figure 14. Sulfide Recovery Versus Time.

Instead diffusion out of the pores and desorption are the mechanisms controlling the removal process. Both of these processes are governed by concentration gradients. Again biological production is a minor source of hydrogen sulfide in the short term, though it becomes increasingly important with increasing time of the experiment.

4.5 Total Sulfur Analysis

Total sulfur tests will determine the total amount of sulfur that exists in the digester sludge. Major sulfur compounds contributing to the total sulfur in the sludge may be sulfate, hydrogen sulfide, methyl mercaptan, dimethyl disulfide and dimethyl sulfide. Tests will be performed to find the relationship between the total sulfur in the solid and liquid portion of the sludge. Depending upon the weather, dry or wet, the total sulfur concentrations in the digester sludge may also vary.

4.6 Floc Size and Diffusion Rate

The size of individual flocs in the digester sludge may be related to the rate of diffusion, digester sulfide concentration and time of year. Experiments will be performed to investigate these relationships.

5. RESULTS AND DISCUSSION

5.1 Modeling of Hydrogen Sulfide Mass Transfer

The mass transfer of hydrogen sulfide from the anaerobic sludge to the gas phase is a function of a multitude of variables. The mass of hydrogen sulfide in the floc and bulk liquid are the two major variables which contribute to the transfer of hydrogen sulfide from one phase to another. The change in floc hydrogen sulfide mass with respect to time is a function of the hydrogen sulfide mass in the floc and in the bulk liquid. As the concentration of hydrogen sulfide in the bulk liquid approaches zero, a greater amount of hydrogen sulfide diffusion occurs from the floc liquid to the bulk liquid. This relationship is shown by equation 31:

$$\frac{dC_f}{dt} = -K_f(C_f - C_b) \qquad (31)$$

Where:

C_f = Hydrogen sulfide mass in floc (mg)

C_b = Hydrogen sulfide mass in bulk liquid (mg)

K_f = Floc constant (s^{-1})

When considering the mass transfer of hydrogen sulfide from the bulk liquid, a conservation of mass analogy can be considered. The change in mass of hydrogen sulfide with respect to time is a function of the mass of hydrogen sulfide leaving the bulk liquid and the mass of hydrogen sulfide entering the bulk liquid from the floc. This relationship is modeled by equation 32:

$$\frac{dC_b}{dt} = K_f(C_f - C_b) - K_b C_b \qquad (32)$$

Where:

K_b = Bulk liquid constant (s^{-1})

Finally, since hydrogen sulfide is a sparingly soluble gas the basic mass transfer relationship can be used. The hydrogen sulfide that exits from the bulk liquid enters the helium bubble, as modeled in equation 33:

$$\frac{dC}{dt} = K_b C_b \qquad (33)$$

All of the above equations are based upon the following underlying assumptions:

$$(C_f)_0 \equiv (C_b)_0 \qquad (34)$$

$$(C_b)_0 \equiv \textit{Gas collected in first } 30 \text{ min}\textit{utes} \qquad (35)$$

The first assumption states that the mass/volume of hydrogen sulfide in the floc at time zero is equal to the mass/volume in the bulk liquid at time zero (prior to any sparging). Equilibrium between the two phases is assumed to be established due to the 17 day detention time of the sludge in the anaerobic digesters. Assumption two states that the mass of hydrogen sulfide in the bulk liquid at time zero is equivalent to the mass of sulfide purged in the first 30 minutes of each experiment.

Equations (31) to (33) were solved simultaneously using a fourth order Runge Kutta method with the initial conditions given by equations (34) and (35). The constants, K_f and K_b, were estimated using a genetic algorithm software package (Sugal) and data from digester 5 and digester 3, as shown in Figure 15. Data used for the calibration of the model were from digester 5, cone level sludge (Figure E6, Appendix E) and digester 3, 7.9 m level sludge (Figure E1, Appendix E):

$K_b = 1.85 \times 10^{-3}\ s^{-1}$

and

$K_f = 4.15 \times 10^{-5}\ s^{-1}$

The above model, with the estimated constants, was verified against data from digester 6, 7.9 m level sludge, digester 5, 7.9 m level sludge, digester 3, 7.9 m level sludge. The observed data and model fit is shown in Figure 16. Residuals between the observed data and the model fit are shown in Figure 17.

In most cases, the residuals between the model predicted values and the observed values were small. Only the data sets from May 14th and 29th are shown to have increasing or decreasing residuals with time. Specifically, considering the data on May 14th, the model over-predicts the rate of sulfide recovery. Prior to May 14th there had been no precipitation in the City of Edmonton for approximately 19 days, thus no scouring of the sewers had occurred. With no precipitation occurring for over 19 days, no settled material in the sewers was conveyed to the treatment plant. As well, when no rain occurs for a significant length of time, the sulfide level in the digester is significantly higher than during times of high runoff. As a result, as shown in Figure 16, on May 14th a significant amount of sulfide is stripped in the first 30 minutes and lower diffusion and desorption occurs thereafter than that which is predicted by the model. Thus, when high sulfide concentrations exist in the digester, more of the available sulfide is recovered in the first portion of the stripping process rather than in the latter portion. This may be the reason for the sulfide recovery from the sludge being slower than usual or lower than the model predicts.

Considering the data from May 29th, the model under-predicts the rate of sulfide recovery (the opposite of what is shown to occur on May 14th). In the days previous and on May 29th, 11 mm of precipitation had fallen in Edmonton (Municipal Airport). This will have led to scouring of the sewers and conveying settled material in the sewers to the treatment plant. During times of high runoff, typically a lower amount of sulfide is recovered during the normal stripping process. This indicates that the addition of the settled material and storm water to the plant may have changed the form of the sulfide ions previously available in the digester or may have inhibited the ability of the sulfide to diffuse and desorb from the sludge. As shown in Figure 16, a lower amount of sulfide is recovered in the first 30 minutes of the stripping process, though a higher rate of sulfide recovery occurs in the latter portion of the process (higher than that predicted by the model).

Therefore, according to Figure 16, the model is adequate in predicting sulfide recovery, although when applying the model to times of high runoff or dry periods the model may under or over predict the actual sulfide levels.

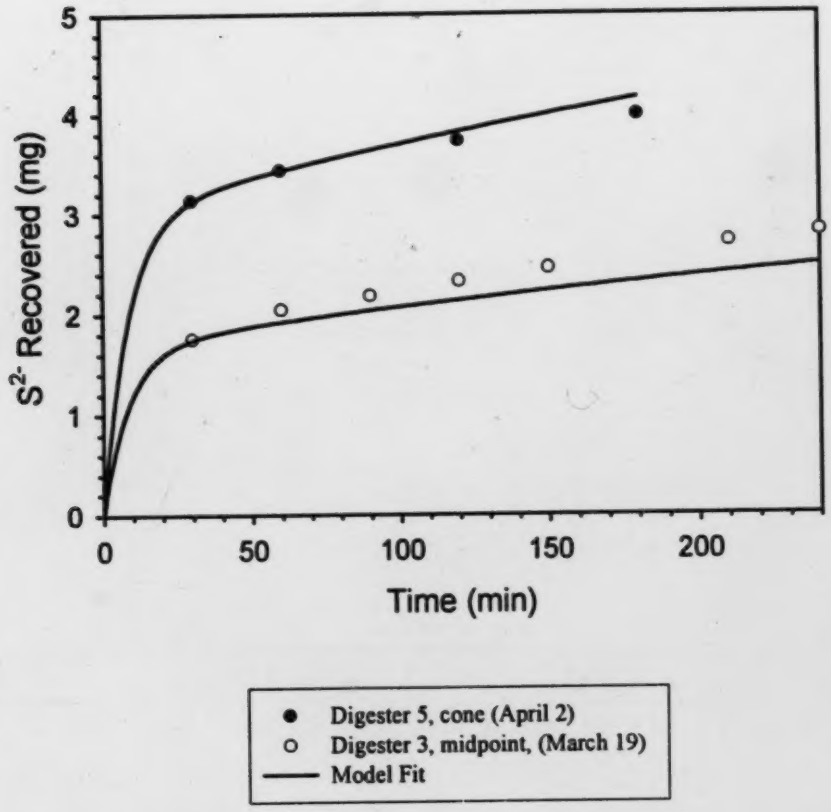

Figure 15. Calibration of Model.

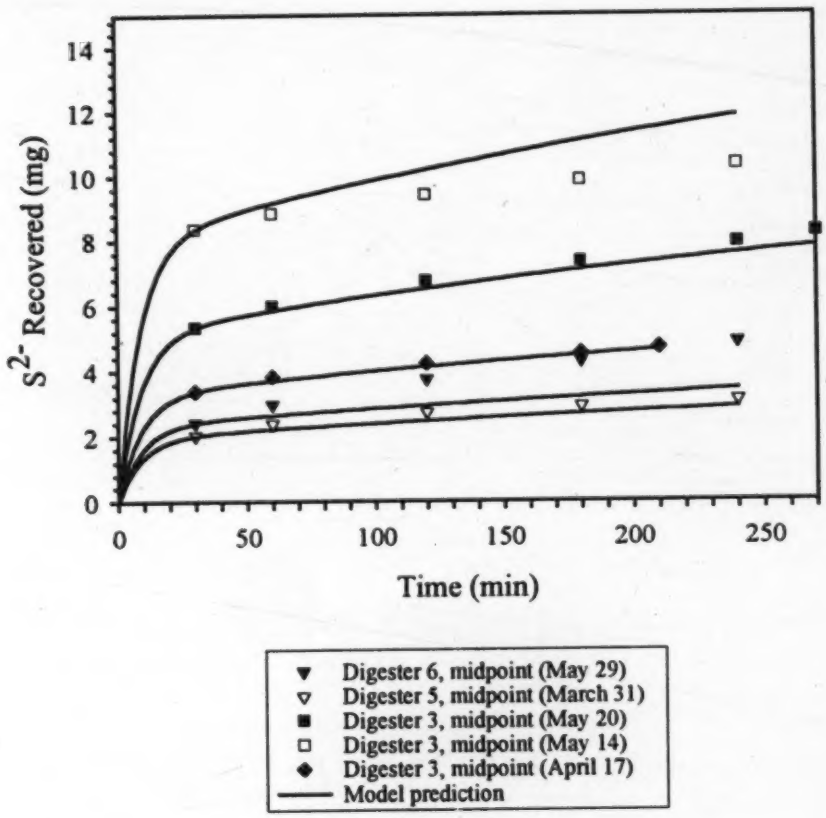

Figure 16. Observed Data and Model Predictions.

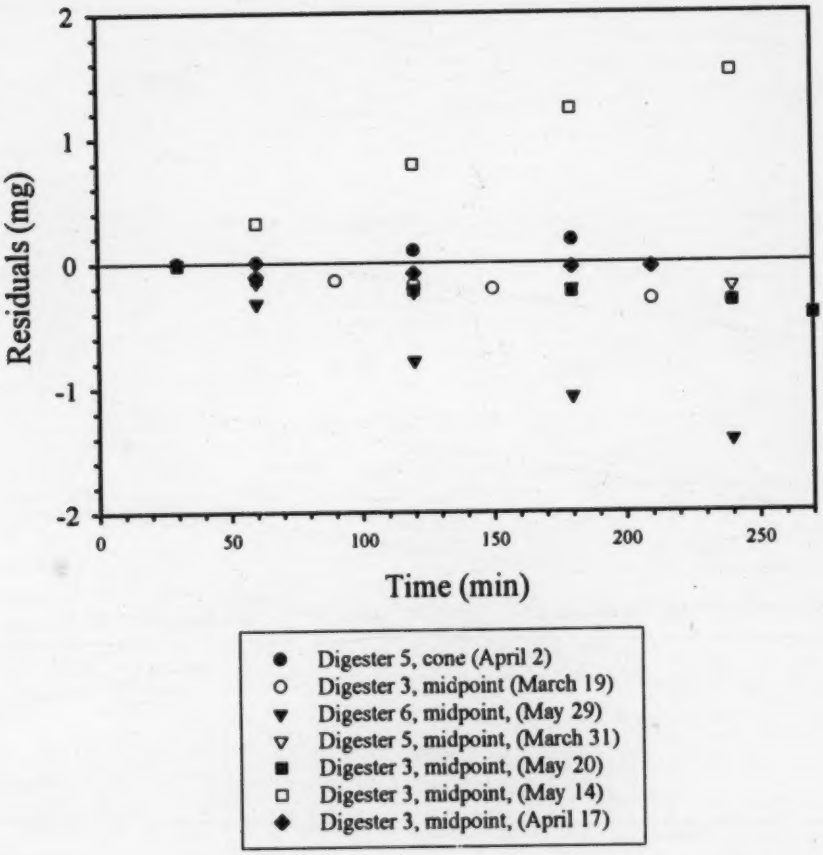

Figure 17. Residuals between the Observed and Model Predicted Data.

5.2 Anaerobic Sludge Analysis

5.2.1 Percent Reduction Versus Chemical Dosages

Typical percent reduction versus dose curves are shown in Figures 18 to 20. These curves show the amount of ferrous or ferric ions required to attain a certain percent reduction in the amount of sulfide originally present in the sludge. All of the percent reduction versus dose curves are shown in Appendix C.

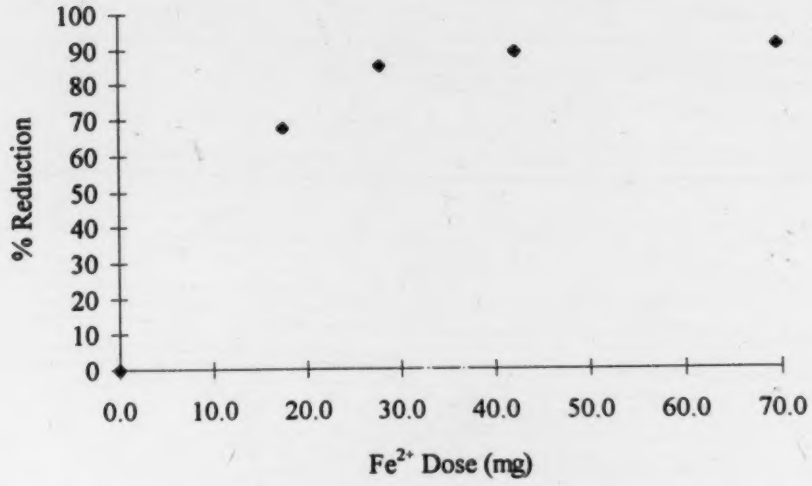

Figure 18. % Reduction vs. Fe^{2+} Dose, Digester 3, 7.9 m
Digester sulfide mass = 6.15 mg (blank).

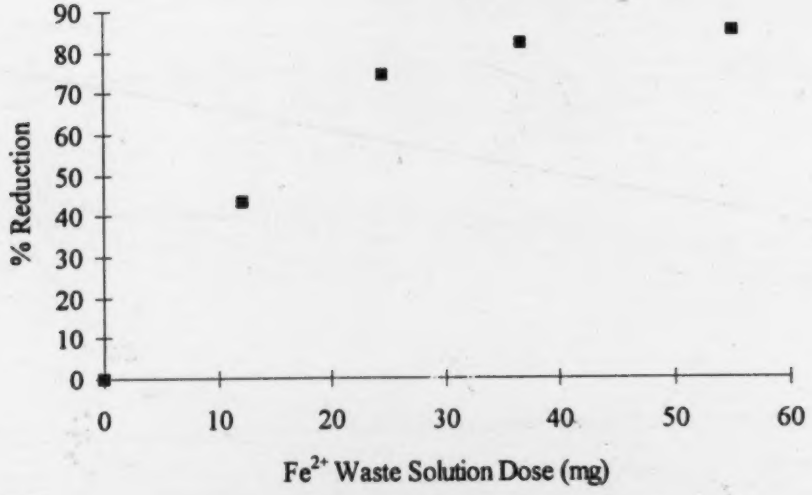

Figure 19. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 3, 7.9 m
Digester sulfide mass = 6.81 mg (blank).

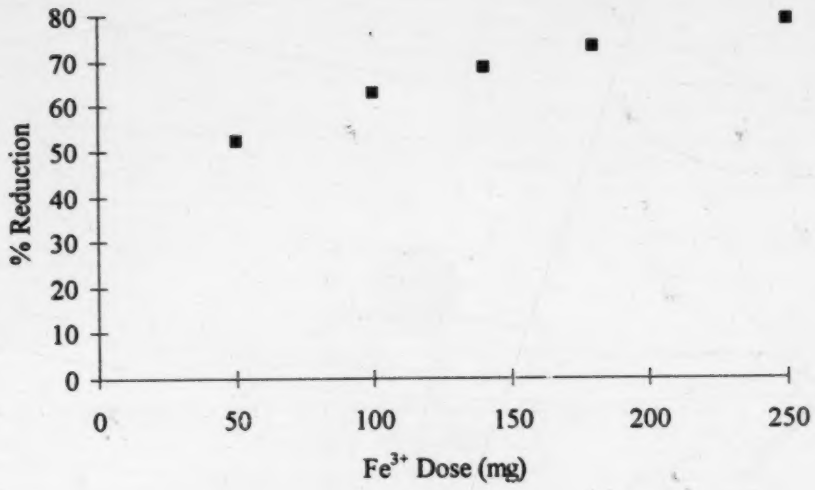

Figure 20. % Reduction vs. Fe^{3+} Dose, Digester 3, 7.9 m
Digester sulfide mass = 5.71 mg (blank).

5.2.2 Percent Reduction Contours

Percent reduction contours were plotted to provide a practical means of treating the sulfide in the digester sludge. Depending upon the amount of sulfide available in the digester and the chemical dose added, a percent reduction of sulfide can be obtained.

Typical percent reduction contours are shown in Figures 21 to 23. Each graph represents the percent reductions obtained when adding one of the three chemicals to a sludge sample from a certain digester and level. See appendix D for all the percent reduction contours.

The reagent grade ferrous chloride and waste ferrous chloride solutions provided the highest percent reductions per amount added. The reagent grade ferric chloride solution provided the lowest percent reduction per dose added. These results are consistent with the theory stated previously in section 4.2.3. The ferric chloride additions provide the lowest efficiency of sulfide removal since the ferric ions must first be reduced to ferrous ions. This is accomplished by the presence of reducing agents such as sulfide. Therefore, lower amounts of sulfide available in the sludge result in fewer ferrous ions forming and precipitating as ferrous sulfide. With the addition of the ferrous chloride reagent grade and ferrous chloride waste solution, no reduction process is required. The ferrous ions are readily available to react with any existing sulfide in the sludge.

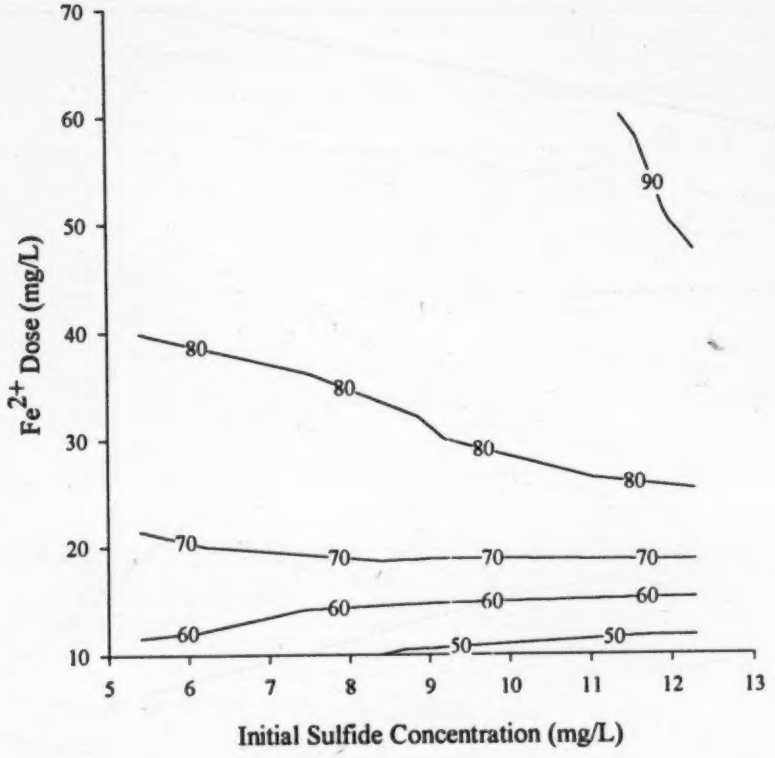

Figure 21. Percent Reduction Contour, Digester 3, 7.9 m level, Fe^{2+} Reagent Grade.

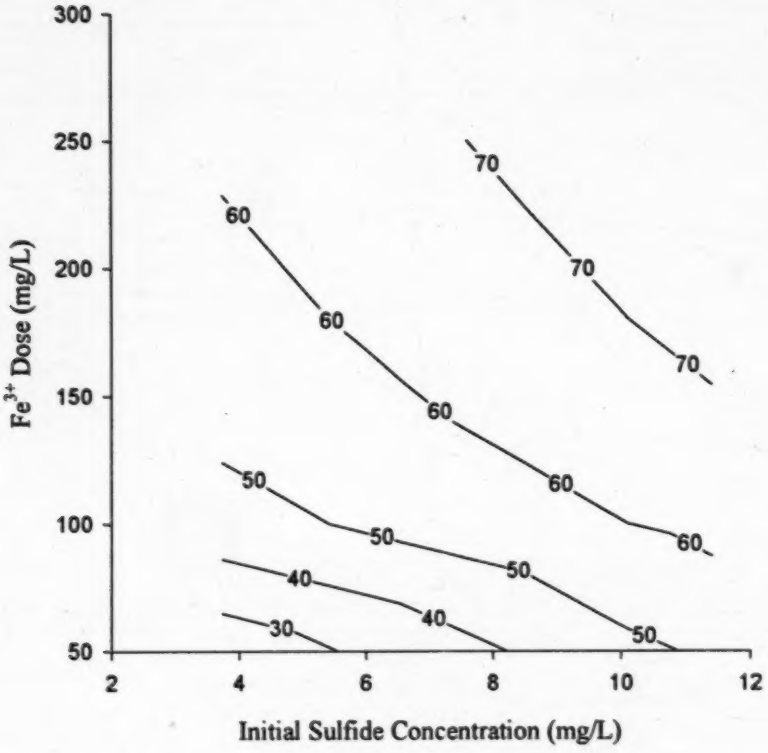

Figure 22. Percent Reduction Contour, Digester 3, 7.9 m level, Fe^{3+} Reagent Grade.

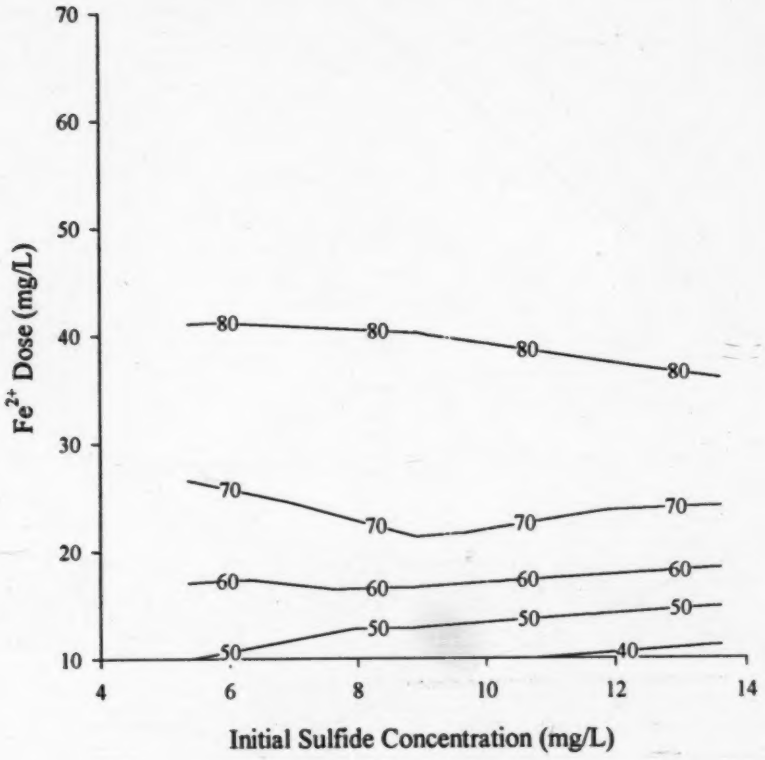

Figure 23. Percent Reduction Contour, Digester 3, 7.9 m level, Fe^{2+} Waste Solution.

5.2.3 Digester Sulfide Concentrations

Depending upon the sampling location in the digester the sulfide concentrations may be different. Due to the differing mixing mechanisms in digesters 3 and 6, sulfide concentrations with respect to height may vary in the two digesters. As stated in section 3.6.3.3, digester 6 has biogas cannon mixers resulting in better mixing than that which is provided in digester 3. Therefore, digester 6 should have a more uniform distribution of sulfide among the different levels, compared to digester 3.

Experimental results contradict the above theory, as a higher degree of uniformity is shown to exist in digester 3 versus digester 6. Considering the sulfide concentrations between the two digesters, performing a 2 sample t-test proves that statistically there is no significant difference between the two digesters. Experimental results are shown in Table 34.

Table 34. Digester Sulfide Concentrations With Respect to Digester Level

Digester	Digester Level	Sparge Time (min)	Mean Sulfide Titrated (mg)	Standard Deviation	Error for 95% confidence
3	11.6 m	30	2.20	0.125	0.199
	7.9 m	30	2.34	0.057	0.091
	Cone	30	2.37	0.066	0.105
6	11.6 m	30	2.11	0.108	0.172
	7.9 m	30	2.62	0.099	0.158
	Cone	30	2.16	0.157	0.250

The source of the sulfide is the liquid and solid portion of the sludge. In digester 3, the lower the level in the digester the higher the concentration of sulfide. This reveals that there may exist a higher amount of sulfide where there is a greater amount of solid

sludge. Since there is better mixing provided in digester 6 a greater amount of solid sludge may exist in the higher levels of the digester. This will result in a greater amount of sulfide existing at the 7.9 m level of digester 6 rather than at the same level of digester 3.

5.2.4 Total Sulfur Analysis

Total sulfur tests were conducted to estimate the amount of sulfur existing in the anaerobic sludge. The total sulfur analyses were performed at Norwest Labs, Edmonton, Canada. Each sample submitted for testing was centrifuged, which separated the liquid and solid portions of the sludge. Total sulfur tests were performed on each of the two phases. The results of the tests are shown in Appendix F. Sample results are shown in Table 35. When the sulfide level in the digester was moderate and high, the total sulfur in the liquid portion of the sludge ranged from 221 to 233 mg/L, and 260 to 460 mg/Kg in the solid portion. Tests performed on a sludge sample that had a low concentration of sulfide showed levels of 235 mg/L of total sulfur in the liquid portion and 910 mg/Kg of total sulfur in the solid portion (as in Appendix F). The concentration of the total sulfur in the solid portion increases substantially during periods of low sulfide levels in the digester. This suggests a higher concentration of sulfur exists in the solid portion of the sludge during high runoff periods (characteristically equating to a low sulfide concentration in the digester sludge). The higher concentration of total sulfur may be due to the increase in flow in the combined sewers and separate sanitary sewers that occurs with runoff. This increases the amount of scouring that occurs in the sewers and conveys any accumulated settled waste to the Gold Bar Wastewater Treatment Plant. Therefore a greater amount

of total sulfur may exist in the solid material that is pumped from the primary tank to the anaerobic digester.

Table 35. Total Sulfur Tests on Digester 3, 7.9 m Sludge, May 20 1998 (Control)

Sparge Time (min)	Phosphate Buffer (mL) pH = 6.7	Chemical Addition (mL)	Sulfide Titrated (mg)	Mean (mg)	Total sulfur in liquid portion (mg/L)	Total sulfur in solid portion (mg/Kg)
30	120	0	5.63			
30	120	0	5.64			
30	120	0	5.59			
30	120	0	5.53	5.60	233	260

As stated previously, a high runoff period substantially decreases the amount of sulfide in the anaerobic digester. Turbulence in sanitary sewers increases during times of high runoff, thus increasing aeration and changing sewer conditions from anaerobic to aerobic. This will lead to the oxidation of sulfide in the wastewater to other compounds such as sulfate.

A typical breakdown of the existing sulfur and other odorous compounds in wastewater is shown in Table F15 of Appendix F.

5.2.5 Floc Size and Diffusion Rate Analysis

Relationships between floc size and digester sulfide concentration, diffusion rate of H_2S from floc to bulk liquid and time were investigated. Diffusion rate being the slope of the straight line portion of the sulfide recovered vs. time graph, as shown in Figure 14. Using a Fisher Scientific Stereomaster microscope, model SPT-ITH, approximate floc widths and lengths were measured. Floc size and diffusion rate analysis results are shown

in Appendix H. No notable relationship could be determined between the floc size and the sulfide digester concentration or diffusion rate.

An apparent relationship between the diffusion rate and the month of the year was shown to exist, as in Figure 24. The diffusion rate was observed to increase from March to May. This may be related to the fact that the amount of measured sulfide steadily increased in the digester over this period, as shown in Figure 25. When higher levels of sulfide are present in the digester sludge, a high concentration of sulfide also exists in the bulk liquid. As the sulfide from the bulk liquid is removed through purging, a high concentration gradient develops between the bulk and floc liquid. Therefore, an increasing sulfide level in the digester sludge will increase the diffusion rate of sulfide from the floc to bulk liquid.

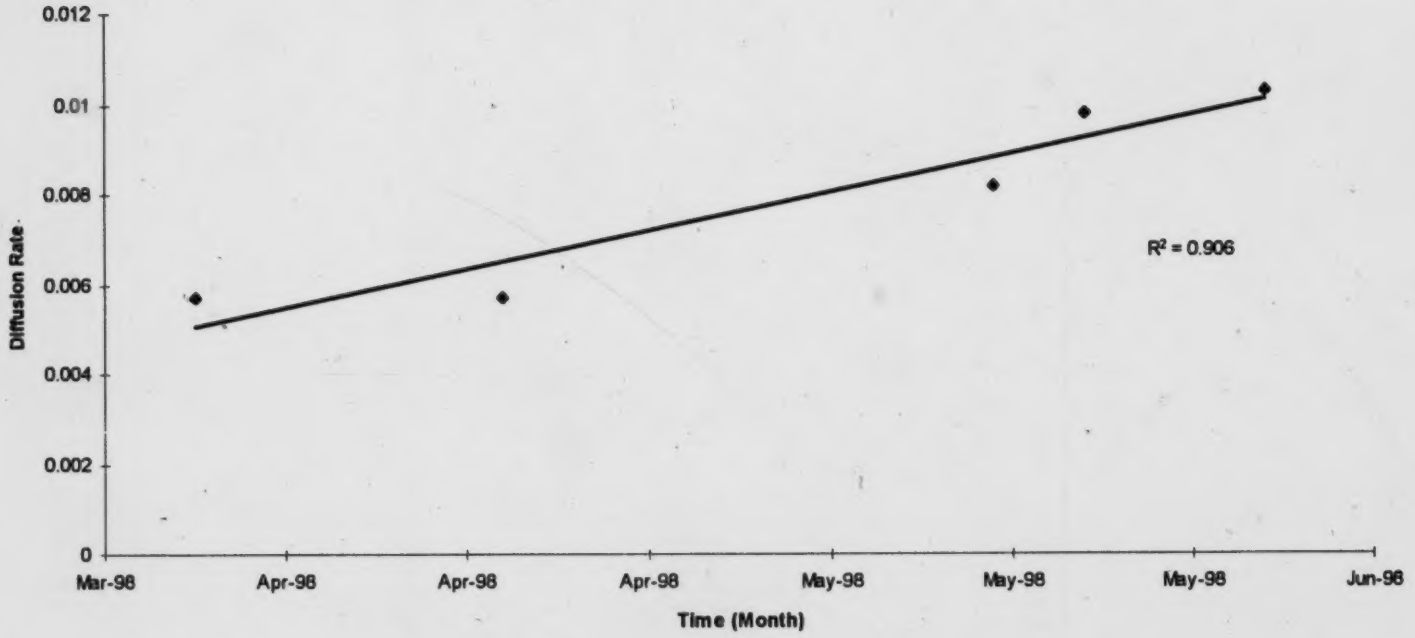

Figure 24. Relationship between Diffusion Rate and Time.

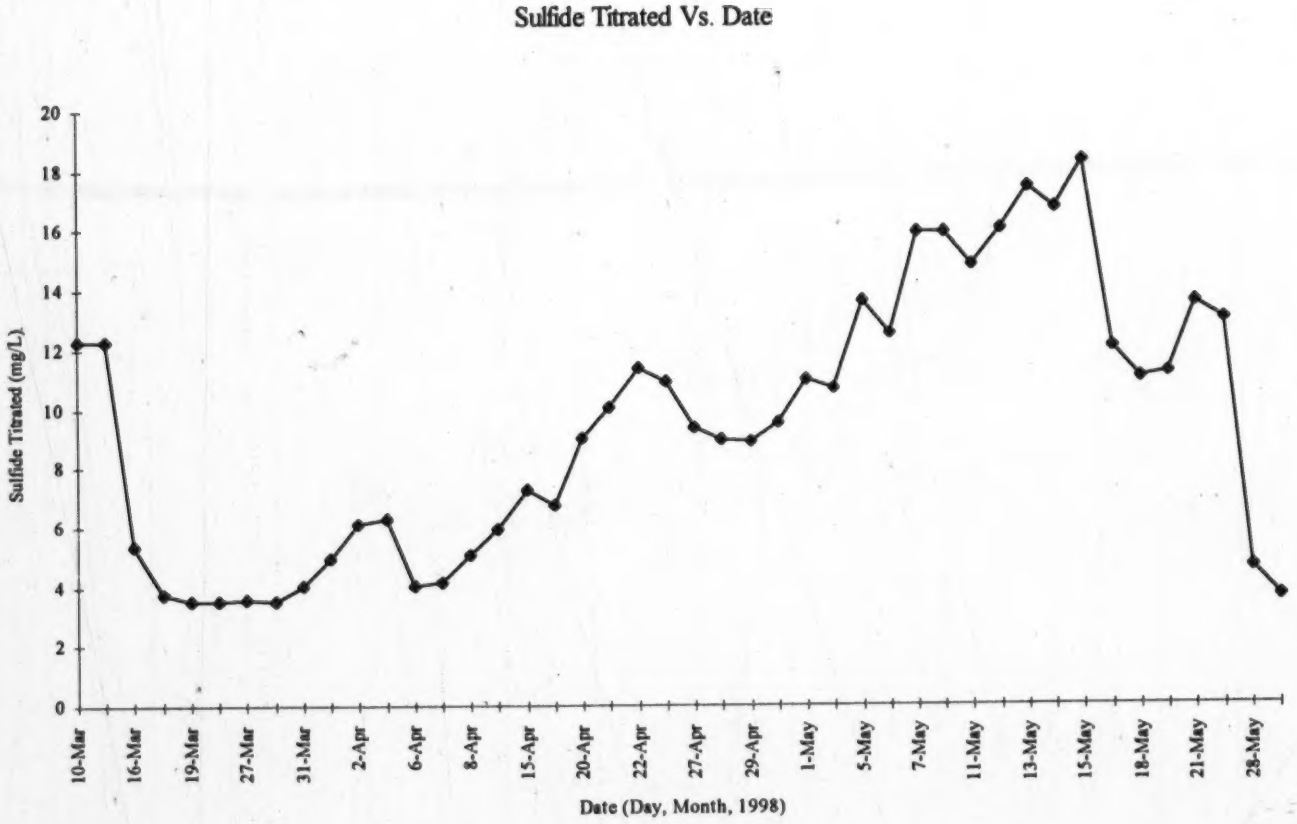

Figure 25. Sulfide Titrated Versus Date.

6. CONCLUSION

Based on the experimental results the following conclusions can be made:

1. Either a $FeCl_2$ reagent grade solution or a $FeCl_2$ waste solution should be added to the anaerobic digester sludge. These chemicals provided the greatest reduction in hydrogen sulfide concentrations with respect to the amount of each chemical added. Depending upon the type and concentration of solution which is chosen, different percent reductions can be obtained. The figures shown in appendix D provide guidelines to the dose of sequestering chemical required to achieve a specified level of hydrogen sulfide removal for a given initial sulfide concentration. $FeCl_3$ was also tested, though provided significantly lower percent reductions with respect to the amount of chemical added.

2. When sparging hydrogen sulfide from the sludge, a majority of the hydrogen sulfide in the bulk liquid portion of the sludge is purged in the first 30 minutes. With continuous sparging there is further diffusion from the bulk liquid to the gas phase, as well as diffusion and desorption of hydrogen sulfide from the interstitial pores and solid portion of the floc to the bulk liquid. The mass transfer of hydrogen sulfide from one phase to another is due to the development of concentration gradients between each of the phases. These concentration gradients drive the transfer of hydrogen sulfide, theoretically leading to the eventual elimination of all hydrogen sulfide in the sludge.

3. The mass transfer of hydrogen sulfide from the solid and liquid phases of the sludge to the gas phase was modeled. The model provided a good indication of sulfide removal with time under most conditions.

4. During periods of high runoff, due to snow melt or rain, a significant decrease in the amount of hydrogen sulfide in the digester is observed. Highest levels of hydrogen sulfide typically exist during fall and winter months, and lowest levels during spring and summer months. The main reason for low sulfide concentrations existing during high runoff periods may be that the sulfide in the incoming wastewater is oxidized to other chemical forms such as sulfate. The unavailability of sulfide leads to the reduced formation of hydrogen sulfide in the liquid and gaseous states. During periods of low runoff, there is a continuous reduction of chemical compounds such as sulfate to sulfide, thus leading to high concentrations of hydrogen sulfide in the liquid and gaseous states. Therefore, weather does have a significant effect on the hydrogen sulfide levels in the digester.

7. RECOMMENDATIONS

In order to further understand and improve the procedures and mechanisms involved in reducing the formation of hydrogen sulfide in the anaerobic digesters, the following recommendations were made for future studies:

1. Ferrous chloride reagent grade and ferrous chloride waste solution additions should be tested on the anaerobic digesters at the Gold Bar Wastewater Treatment Plant. Hydrogen sulfide concentrations should be measured before and after the treatment to provide a relationship between chemical dose and percent reduction.

2. Investigation of the optimum point to add the chemical at the plant would be beneficial to explore. Additions to different areas, such as the primaries or directly to the digester, may provide different degrees of odor and corrosion control.

3. Depending upon the location of the chemical addition, some downstream processes or equipment may be affected by the presence of the ferrous ions. Experiments ensuring the ferrous concentrations are not severely inhibiting any processes or equipment are necessary. The resultant information would provide valuable data in assessing whether it is economically feasible to add such a chemical product.

4. Tests can be conducted on the anaerobic sludge to identify the specific types of sulfur species present. Such tests performed before and after periods of high runoff, will show the types of sulfur species and concentrations existing within the sludge during dry and wet periods.

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APPENDIX A. Raw Data of Chemical Additions to Digesters 3 and 6 (7.9 m Level Sludge)

Table A1. Ferrous chloride reagent grade additions to digester 3, 7.9 m sludge

Date of Experiment: March 10 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ $4H_2O$ (5g/L) (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	6.07				
30	120	0	0.0	6.27				
30	120	0	0.0	5.95				
30	120	0	0.0	6.29	6.15	0.162	0.257	0
30	120	6.2	17.4	2.18				
30	120	6.2	17.4	2.09				
30	120	6.2	17.4	1.98				
30	120	6.2	17.4	1.69	1.99	0.215	0.342	67.6
30	120	9.9	27.8	0.79				
30	120	9.9	27.8	0.97				
30	120	9.9	27.8	1.16				
30	120	9.9	27.8	0.79	0.93	0.177	0.282	84.9
30	120	15	42.1	0.75				
30	120	15	42.1	0.57				
30	120	15	42.1	0.59				
30	120	15	42.1	0.78	0.67	0.105	0.167	89.1
30	120	24.8	69.7	0.57				
30	120	24.8	69.7	0.46				
30	120	24.8	69.7	0.61				
30	120	24.8	69.7	0.66	0.58	0.084	0.134	90.7

Table A2. Ferric chloride reagent grade additions to digester 3, 7.9 m sludge

Date of Experiment: March 12 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_3$ $6H_2O$ (5g/L) (mL)	As Fe^{3+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)	% Error Percent Reduction (+ or -)
30	120	0	0.0	5.13					
30	120	0	0.0	6.29	5.71	0.817	-	0.000	-
30	120	20	41.3	3.50					
30	120	20	41.3	2.50					
30	120	20	41.3	3.45					
30	120	20	41.3	2.61	3.01	0.535	0.851	47.2	14.8
30	120	35	72.3	2.58					
30	120	35	72.3	2.26					
30	120	35	72.3	2.74					
30	120	35	72.3	2.30	2.47	0.227	0.361	56.8	6.3
30	120	50	103.3	1.80					
30	120	50	103.3	1.67					
30	120	50	103.3	2.68					
30	120	50	103.3	2.07	2.06	0.452	0.719	64.0	12.6
30	120	65	134.3	1.80					
30	120	65	134.3	1.46					
30	120	65	134.3	1.94					
30	120	65	134.3	2.14	1.84	0.286	0.455	67.8	7.97
30	120	130	268.6	1.24					
30	120	130	268.6	1.13	1.18	0.078	0.699	79.3	12.2

Table A3. Ferrous chloride waste solution additions to digester 3, 7.9 m sludge

Date of Experiment: March 16 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Average Percent Reduction (%)
30	120	0	0.0	2.53		
30	120	0	0.0	2.74		
30	120	0	0.0	2.65		
30	120	0	0.0	2.78	2.68	0.0
30	120	2	6.1	1.93		
30	120	2	6.1	2.22		
30	120	2	6.1	1.34		
30	120	2	6.1	1.36	1.71	36.1
30	120	5	15.3	1.23		
30	120	5	15.3	0.86		
30	120	5	15.3	0.99		
30	120	5	15.3	1.39	1.12	58.3
30	120	10	30.6	0.62		
30	120	10	30.6	0.58		
30	120	10	30.6	0.78		
30	120	10	30.6	0.89	0.72	73.3
30	120	15	45.9	0.44		
30	120	15	45.9	0.37		
30	120	15	45.9	0.51		
30	120	15	45.9	0.53	0.46	82.7

Table A4. Ferrous chloride reagent grade additions to digester 3, 7.9 m sludge

Date of Experiment: March 17 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ $4H_2O$ 5g/L (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0	2.65				
30	120	0	0	2.78				
30	120	0	0	2.61				
30	120	0	0	2.74	2.70	0.078	0.123	0
30	120	3	8.4	1.18				
30	120	3	8.4	1.27				
30	120	3	8.4	1.29	1.25	0.061	0.151	53.8
30	120	5	14.1	0.87				
30	120	5	14.1	1.10				
30	120	5	14.1	1.09	1.02	0.131	0.324	62.1
30	120	7.5	21.1	0.57				
30	120	7.5	21.1	0.88				
30	120	7.5	21.1	0.78	0.74	0.158	0.394	72.5
30	120	12	33.7	0.69				
30	120	12	33.7	0.62				
30	120	12	33.7	0.63	0.64	0.037	0.093	76.1

Table A5. Ferric chloride reagent grade additions to digester 3, 7.9 m sludge

Date of Experiment: March 18 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_3$ $6H_2O$ (5g/L) (mL)	As Fe^{3+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	1.89				
30	120	0	0.0	1.48				
30	120	0	0.0	2.05				
30	120	0	0.0	2.05	1.87	0.268	0.427	0.00
30	120	50	103.3	1.50				
30	120	50	103.3	1.43				
30	120	50	103.3	1.28	1.40	0.109	0.272	48.0
30	120	75	155.0	1.13				
30	120	75	155.0	1.32				
30	120	75	155.0	1.32	1.26	0.111	0.277	53.3
30	120	100	206.6	1.66				
30	120	100	206.6	0.76				
30	120	100	206.6	0.90	1.11	0.484	1.203	59.0

Table A6. Ferric chloride reagent grade additions to digester 6, 7.9 m sludge

Date of Experiment: March 26 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_3$ $6H_2O$ (10g/L) (mL)	$FeCl_3$ (mg/L)	As Fe^{3+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	0.0	1.95				
30	120	0	0.0	0.0	1.64				
30	120	0	0.0	0.0	1.90				
30	120	0	0.0	0.0	1.50	1.75	0.213	0.339	0.0
30	120	15	180.0	62.0	1.37				
30	120	15	180.0	62.0	1.43				
30	120	15	180.0	62.0	0.92				
30	120	15	180.0	62.0	1.59	1.33	0.288	0.458	24.0
30	120	30	360.0	124.0	1.23				
30	120	30	360.0	124.0	1.06				
30	120	30	360.0	124.0	1.07				
30	120	30	360.0	124.0	1.13	1.12	0.079	0.125	35.9
30	120	50	600.1	206.6	0.90				
30	120	50	600.1	206.6	0.92				
30	120	50	600.1	206.6	0.87				
30	120	50	600.1	206.6	1.00	0.92	0.056	0.090	47.1
30	120	80	960.1	330.6	0.84				
30	120	80	960.1	330.6	0.86				
30	120	80	960.1	330.6	0.54				
30	120	80	960.1	330.6	1.06	0.83	0.216	0.344	52.8

Table A7. Ferrous chloride reagent grade additions to digester 6, 7.9 m sludge

Date of Experiment: March 27 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2\ 4H_2O$ (5g/L) (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	1.90				
30	120	0	0.0	1.50				
30	120	0	0.0	1.71				
30	120	0	0.0	2.04	1.79	0.234	0.373	0
30	120	3	8.4	1.02				
30	120	3	8.4	1.31				
30	120	3	8.4	1.10				
30	120	3	8.4	1.12	1.14	0.123	0.196	36.3
30	120	6	16.9	0.77				
30	120	6	16.9	0.67				
30	120	6	16.9	0.72				
30	120	6	16.9	0.72	0.72	0.040	0.063	59.7
30	120	10	28.1	0.65				
30	120	10	28.1	0.66				
30	120	10	28.1	0.49				
30	120	10	28.1	0.64	0.61	0.080	0.128	65.8
30	120	13	36.5	0.59				
30	120	13	36.5	0.52				
30	120	13	36.5	0.48				
30	120	13	36.5	0.59	0.54	0.055	0.088	69.6

Table A8. Ferrous chloride waste solution additions to digester 6, 7.9 m sludge

Date of Experiment: March 28 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0	1.71				
30	120	0	0	2.04				
30	120	0	0	1.74				
30	120	0	0	1.59	1.77	0.193	0.307	0.0
30	120	5	15.3	0.89				
30	120	5	15.3	0.83				
30	120	5	15.3	0.92				
30	120	5	15.3	0.70	0.83	0.096	0.152	52.9
30	120	7.5	22.95	0.69				
30	120	7.5	22.95	0.50				
30	120	7.5	22.95	0.55				
30	120	7.5	22.95	0.57	0.58	0.081	0.129	67.3
30	120	10	30.6	0.47				
30	120	10	30.6	0.67				
30	120	10	30.6	0.69				
30	120	10	30.6	0.62	0.61	0.101	0.160	65.3
30	120	15	45.9	0.47				
30	120	15	45.9	0.50				
30	120	15	45.9	0.52				
30	120	15	45.9	0.50	0.50	0.018	0.028	71.8
30	120	20	61.2	0.49				
30	120	20	61.2	0.54	0.52	0.037	0.330	70.7

Table A9. Ferrous chloride waste solution additions to digester 6, 7.9 m sludge

Date of Experiment: April 14 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0	3.27				
30	120	0	0	2.73				
30	120	0	0	2.85				
30	120	0	0	3.05	2.97	0.237	0.377	0.0
30	120	3.5	10.7	0.98				
30	120	3.5	10.7	1.42				
30	120	3.5	10.7	1.29	1.23	0.226	0.562	58.8
30	120	5	15.3	0.85				
30	120	5	15.3	0.86				
30	120	5	15.3	0.95				
30	120	5	15.3	0.97	0.91	0.059	0.094	69.5
30	120	7.5	23.0	0.68				
30	120	7.5	23.0	0.63				
30	120	7.5	23.0	0.55				
30	120	7.5	23.0	0.79	0.66	0.103	0.163	77.7
30	120	10	30.6	0.57				
30	120	10	30.6	0.41				
30	120	10	30.6	0.69	0.56	0.140	0.348	81.2

Table A10. Ferrous chloride reagent grade additions to digester 6, 7.9 m sludge

Date of Experiment: April 15 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ $4H_2O$ (5g/L) (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	3.48				
30	120	0	0.0	3.28				
30	120	0	0.0	3.45				
30	120	0	0.0	4.34	3.64	0.477	0.758	0
30	120	6	16.9	1.18				
30	120	6	16.9	1.08				
30	120	6	16.9	1.33				
30	120	6	16.9	1.47	1.26	0.168	0.267	65.3
30	120	10	28.1	0.72				
30	120	10	28.1	0.77				
30	120	10	28.1	0.68				
30	120	10	28.1	0.72	0.72	0.034	0.054	80.1
30	120	13	36.5	0.75				
30	120	13	36.5	0.68				
30	120	13	36.5	0.56				
30	120	13	36.5	0.86	0.71	0.126	0.201	80.4
30	120	20	56.2	0.52				
30	120	20	56.2	0.74				
30	120	20	56.2	0.50				
30	120	20	56.2	0.80	0.64	0.154	0.244	82.4

Table A11. Ferrous chloride reagent grade additions to digester 6, 7.9 m sludge

Date of Experiment: April 21 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ $4H_2O$ (5g/L) (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0	4.88				
30	120	0	0	4.55				
30	120	0	0	5.12				
30	120	0	0	5.49	5.01	0.397	0.630	0.0
30	120	5	14.0	1.64				
30	120	5	14.0	1.69				
30	120	5	14.0	1.39				
30	120	5	14.0	2.26	1.74	0.366	0.581	65.2
30	120	9	25.3	0.97				
30	120	9	25.3	0.85				
30	120	9	25.3	1.20				
30	120	9	25.3	1.25	1.07	0.188	0.299	78.7
30	120	13	36.5	0.93				
30	120	13	36.5	0.90				
30	120	13	36.5	0.85				
30	120	13	36.5	1.17	0.96	0.144	0.229	80.8
30	120	20	56.2	0.63				
30	120	20	56.2	0.80				
30	120	20	56.2	0.67				
30	120	20	56.2	0.81	0.73	0.090	0.143	85.5

Table A12. Ferrous chloride waste solution additions to digester 6, 7.9 m sludge

Date of Experiment: April 23 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0	5.81				
30	120	0	0	5.78				
30	120	0	0	5.39				
30	120	0	0	4.76	5.44	0.488	0.776	0
30	120	6	18.4	2.27				
30	120	6	18.4	1.76				
30	120	6	18.4	2.18				
30	120	6	18.4	1.48	1.93	0.370	0.588	64.6
30	120	8	24.5	1.79				
30	120	8	24.5	1.48				
30	120	8	24.5	1.80				
30	120	8	24.5	1.24	1.58	0.273	0.434	71.0
30	120	13	39.8	0.91				
30	120	13	39.8	0.69				
30	120	13	39.8	0.51				
30	120	13	39.8	0.89	0.75	0.191	0.303	86.2
30	120	20	61.2	0.68				
30	120	20	61.2	0.54				
30	120	20	61.2	0.62	0.62	0.070	0.174	88.7

Table A13. Ferrous chloride waste solution additions to digester 6, 7.9 m sludge

Date of Experiment: April 27 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average % Reduction	% Error for Percent Reduction (+ or -)
30	120	0	0	4.81					
30	120	0	0	4.27					
30	120	0	0	4.31					
30	120	0	0	5.33	4.68	0.498	0.791	0	16.9
30	120	5	15.3	1.84					
30	120	5	15.3	2.04					
30	120	5	15.3	2.05					
30	120	5	15.3	1.97	1.98	0.095	0.151	57.8	3.2
30	120	8	24.5	0.95					
30	120	8	24.5	1.28					
30	120	8	24.5	1.33					
30	120	8	24.5	1.07	1.16	0.177	0.281	75.3	6.0
30	120	12	36.7	0.72					
30	120	12	36.7	1.17					
30	120	12	36.7	0.91					
30	120	12	36.7	0.72	0.88	0.213	0.338	81.2	7.2
30	120	18	55.1	0.64					
30	120	18	55.1	0.84					
30	120	18	55.1	0.75					
30	120	18	55.1	0.80	0.76	0.087	0.138	83.8	2.9

Table A14. Ferrous chloride waste solution additions to digester 3, 7.9 m sludge

Date of Experiment: April 28 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average % Reduction	% Error for Percent Reduction (+ or -)
30	120	0	0	4.77					
30	120	0	0	4.53					
30	120	0	0	4.18					
30	120	0	0	4.36	4.46	0.251	0.399	0	8.9
30	120	4	12.2	2.24					
30	120	4	12.2	2.19					
30	120	4	12.2	2.15					
30	120	4	12.2	2.43	2.25	0.123	0.195	49.6	4.4
30	120	7	21.4	1.22					
30	120	7	21.4	1.53					
30	120	7	21.4	1.05	1.27	0.243	0.605	71.6	13.6
30	120	12	36.7	0.88					
30	120	12	36.7	0.81					
30	120	12	36.7	0.95					
30	120	12	36.7	0.83	0.87	0.061	0.098	80.6	2.2
30	120	17	52.0	0.72					
30	120	17	52.0	0.81					
30	120	17	52.0	0.95					
30	120	17	52.0	0.72	0.80	0.110	0.175	82.1	3.9

Table A15. Ferrous chloride reagent grade additions to digester 3, 7.9 m sludge

Date of Experiment: April 29 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ $4H_2O$ (5g/L) (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average % Reduction	% Error Percent Reduction (+ or -)
30	120	0	0.0	4.31					
30	120	0	0.0	4.07					
30	120	0	0.0	4.77					
30	120	0	0.0	4.61	4.44	0.310	0.493	0	11.1
30	120	5	14.0	1.59					
30	120	5	14.0	1.72					
30	120	5	14.0	1.57					
30	120	5	14.0	1.97	1.71	0.184	0.293	61.4	6.6
30	120	8	22.5	0.87					
30	120	8	22.5	1.33					
30	120	8	22.5	1.08					
30	120	8	22.5	1.11	1.10	0.187	0.297	75.3	6.7
30	120	12	33.7	0.75					
30	120	12	33.7	0.88					
30	120	12	33.7	0.68					
30	120	12	33.7	0.73	0.76	0.087	0.138	82.8	3.1
30	120	18	50.6	0.64					
30	120	18	50.6	0.69					
30	120	18	50.6	0.81					
30	120	18	50.6	0.76	0.72	0.074	0.118	83.7	2.7

Table A16. Ferric chloride reagent grade additions to digester 6, 7.9 m sludge

Date of Experiment: May 4 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_3$ $6H_2O$ (10g/L) (mL)	As Fe^{3+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0	5.82				
30	120	0	0	5.15				
30	120	0	0	5.18				
30	120	0	0	5.14	5.32	0.331	0.526	0
30	120	12	49.6	1.86				
30	120	12	49.6	2.41				
30	120	12	49.6	2.13				
30	120	12	49.6	2.05	2.11	0.231	0.367	60.3
30	120	25	103.3	1.47				
30	120	25	103.3	1.78				
30	120	25	103.3	1.74				
30	120	25	103.3	1.68	1.67	0.139	0.221	68.7
30	120	40	165.3	1.66				
30	120	40	165.3	1.56				
30	120	40	165.3	1.46				
30	120	40	165.3	1.86	1.64	0.170	0.270	69.3
30	120	60	247.9	1.22				
30	120	60	247.9	1.54				
30	120	60	247.9	1.55				
30	120	60	247.9	1.75	1.51	0.220	0.350	71.5

Table A17. Ferrous chloride waste solution additions to digester 3, 7.9 m sludge

Date of Experiment: May 5 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average % Reduction	% Error for Percent Reduction (+ or -)
30	120	0	0	6.38					
30	120	0	0	6.53					
30	120	0	0	6.99					
30	120	0	0	7.35	6.81	0.443	0.704	0	10.3
30	120	4	12.24	3.71					
30	120	4	12.24	4.10					
30	120	4	12.24	3.75					
30	120	4	12.24	3.81	3.84	0.178	0.283	43.6	4.2
30	120	8	24.48	1.99					
30	120	8	24.48	1.58					
30	120	8	24.48	1.80					
30	120	8	24.48	1.62	1.75	0.188	0.300	74.3	4.4
30	120	12	36.72	1.20					
30	120	12	36.72	1.01					
30	120	12	36.72	1.39					
30	120	12	36.72	1.27	1.22	0.158	0.252	82.1	3.7
30	120	18	55.08	0.84					
30	120	18	55.08	1.15					
30	120	18	55.08	0.93					
30	120	18	55.08	1.20	1.03	0.174	0.277	84.9	4.1

Table A18. Ferrous chloride reagent grade additions to digester 6, 7.9 m sludge

Date of Experiment: May 6 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ $4H_2O$ (5g/L) (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0	7.01				
30	120	0	0	6.40				
30	120	0	0	5.22				
30	120	0	0	6.45	6.27	0.752	1.195	0
30	120	4	11.2	3.95				
30	120	4	11.2	3.53				
30	120	4	11.2	3.51				
30	120	4	11.2	3.40	3.60	0.242	0.385	42.6
30	120	7	19.7	2.15				
30	120	7	19.7	2.15				
30	120	7	19.7	2.01				
30	120	7	19.7	1.65	1.99	0.238	0.378	68.3
30	120	11	30.9	1.21				
30	120	11	30.9	1.17				
30	120	11	30.9	0.88				
30	120	11	30.9	1.21	1.12	0.158	0.252	82.2
30	120	18	50.6	0.75				
30	120	18	50.6	0.81				
30	120	18	50.6	0.70				
30	120	18	50.6	0.70	0.74	0.049	0.078	88.2

Table A19. Ferric chloride reagent grade additions to digester 6, 7.9 m sludge

Date of Experiment: May 11 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_3$ $6H_2O$ (10g/L) (mL)	As Fe^{3+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)	% Error Percent Reduction (+ or -)
30	120	0	0	7.21					
30	120	0	0	7.52					
30	120	0	0	7.29					
30	120	0	0	7.62	7.41	0.191	0.304	0	4.1
30	120	12	49.6	1.82					
30	120	12	49.6	3.00					
30	120	12	49.6	2.28					
30	120	12	49.6	2.41	2.38	0.488	0.776	67.9	10.5
30	120	25	103.3	1.73					
30	120	25	103.3	1.58					
30	120	25	103.3	2.57					
30	120	25	103.3	1.89	1.94	0.437	0.694	73.8	9.4
30	120	40	165.3	1.82					
30	120	40	165.3	1.76					
30	120	40	165.3	2.05					
30	120	40	165.3	1.97	1.90	0.134	0.213	74.4	2.9
30	120	70	289.3	1.14					
30	120	70	289.3	1.95					
30	120	70	289.3	1.59					
30	120	70	289.3	1.92	1.65	0.375	0.597	77.7	8.1

Table A20. Ferrous chloride waste solution additions to digester 6, 7.9 m sludge

Date of Experiment: May 16 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0	6.03				
30	120	0	0	5.53				
30	120	0	0	6.16				
30	120	0	0	6.43	6.04	0.380	0.604	0
30	120	7	21.4	2.36				
30	120	7	21.4	1.70				
30	120	7	21.4	2.14				
30	120	7	21.4	2.03	2.06	0.277	0.440	65.9
30	120	10	30.6	1.23				
30	120	10	30.6	1.36				
30	120	10	30.6	1.15				
30	120	10	30.6	1.57	1.33	0.186	0.296	78.0
30	120	14	42.8	1.22				
30	120	14	42.8	0.97				
30	120	14	42.8	0.97				
30	120	14	42.8	1.20	1.09	0.137	0.218	82.0
30	120	20	61.2	0.87				
30	120	20	61.2	0.89				
30	120	20	61.2	0.81	0.86	0.0394	0.0979	85.9

APPENDIX B. Raw Data of Chemical Additions to Digesters 3 and 6 (Cone Level Sludge)

Table B1. Ferrous chloride reagent grade additions to digester 3, cone sludge

Date of Experiment: April 1 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2 4H_20$ (5g/L) (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	2.51				
30	120	0	0.0	2.68				
30	120	0	0.0	2.61				
30	120	0	0.0	2.12	2.48	0.250	0.398	0
30	120	6	16.9	0.96				
30	120	6	16.9	0.98				
30	120	6	16.9	0.66				
30	120	6	16.9	0.72	0.83	0.165	0.262	66.5
30	120	10	28.1	0.62				
30	120	10	28.1	0.71				
30	120	10	28.1	0.73				
30	120	10	28.1	0.43	0.62	0.138	0.220	74.9
30	120	13	36.5	0.45				
30	120	13	36.5	0.73				
30	120	13	36.5	0.52				
30	120	13	36.5	0.55	0.56	0.120	0.189	77.4
30	120	20	56.2	0.41				
30	120	20	56.2	0.36				
30	120	20	56.2	0.36				
30	120	20	56.2	0.27	0.35	0.056	0.089	85.9

Table B2. Ferrous chloride reagent grade additions to digester 6, cone sludge

Date of Experiment: April 2 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2\ 4H_20$ (5g/L) (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	3.19				
30	120	0	0.0	3.01				
30	120	0	0.0	2.91				
30	120	0	0.0	3.15	3.06	0.125	0.199	0
30	120	6	16.9	0.70				
30	120	6	16.9	0.59				
30	120	6	16.9	0.67				
30	120	6	16.9	0.84	0.70	0.103	0.164	77.1
30	120	10	28.1	0.84				
30	120	10	28.1	0.68				
30	120	10	28.1	0.55				
30	120	10	28.1	0.24	0.58	0.251	0.399	81.2
30	120	13	36.5	0.68				
30	120	13	36.5	0.51				
30	120	13	36.5	0.52				
30	120	13	36.5	0.68	0.60	0.094	0.150	80.5
30	120	20	56.2	0.50				
30	120	20	56.2	0.41				
30	120	20	56.2	0.38				
30	120	20	56.2	0.12	0.35	0.160	0.254	88.5

Table B3. Ferrous chloride waste solution additions to digester 6, cone sludge

Date of Experiment: April 3 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	3.37				
30	120	0	0.0	2.79				
30	120	0	0.0	3.29	3.15	0.312	0.776	0
30	120	5	15.3	0.99				
30	120	5	15.3	1.12				
30	120	5	15.3	1.30				
30	120	5	15.3	1.21	1.16	0.130	0.206	63.3
30	120	7.5	23.0	1.05				
30	120	7.5	23.0	0.97				
30	120	7.5	23.0	1.11				
30	120	7.5	23.0	1.12	1.06	0.072	0.115	66.2
30	120	10	30.6	0.93				
30	120	10	30.6	0.92				
30	120	10	30.6	0.61				
30	120	10	30.6	0.42	0.72	0.250	0.398	77.2
30	120	15	45.9	0.56				
30	120	15	45.9	0.61				
30	120	15	45.9	0.58				
30	120	15	45.9	0.49	0.56	0.048	0.077	82.2

Table B4. Ferrous chloride waste solution additions to digester 3, cone sludge

Date of Experiment: April 6 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	1.79				
30	120	0	0.0	2.05				
30	120	0	0.0	2.01				
30	120	0	0.0	2.28	2.03	0.202	0.321	0
30	120	5	15.3	1.23				
30	120	5	15.3	0.89				
30	120	5	15.3	1.21	1.11	0.191	0.475	45.4
30	120	7.5	23.0	0.87				
30	120	7.5	23.0	0.62				
30	120	7.5	23.0	0.66				
30	120	7.5	23.0	0.75	0.73	0.109	0.174	64.3
30	120	10	30.6	0.48				
30	120	10	30.6	0.57				
30	120	10	30.6	0.63				
30	120	10	30.6	0.59	0.57	0.060	0.096	72.2
30	120	15	45.9	0.43				
30	120	15	45.9	0.52				
30	120	15	45.9	0.58				
30	120	15	45.9	0.52	0.51	0.064	0.102	74.7

Table B5. Ferric chloride reagent grade additions to digester 3, cone sludge

Date of Experiment: April 7 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_3 6H_20$ (10g/L) (mL)	As Fe^{3+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	2.08				
30	120	0	0.0	2.27				
30	120	0	0.0	2.02				
30	120	0	0.0	1.94	2.08	0.137	0.218	0
30	120	15	62.0	1.39				
30	120	15	62.0	1.27				
30	120	15	62.0	1.43				
30	120	15	62.0	1.31	1.35	0.071	0.114	35.0
30	120	30	124.0	1.12				
30	120	30	124.0	1.02				
30	120	30	124.0	0.99				
30	120	30	124.0	0.87	1.00	0.104	0.165	51.8
30	120	50	206.6	0.84				
30	120	50	206.6	0.45				
30	120	50	206.6	0.58				
30	120	50	206.6	0.53	0.60	0.169	0.269	71.3
30	120	80	330.6	0.64				
30	120	80	330.6	0.47				
30	120	80	330.6	0.29				
30	120	80	330.6	0.38	0.45	0.151	0.240	78.6

Table B6. Ferric chloride reagent grade additions to digester 6, cone sludge

Date of Experiment: April 8 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_3$ $6H_20$ 10g/L (mL)	As Fe^{3+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	2.49				
30	120	0	0.0	2.50				
30	120	0	0.0	2.46				
30	120	0	0.0	2.73	2.54	0.123	0.195	0
30	120	20	82.6	1.63				
30	120	20	82.6	1.72				
30	120	20	82.6	1.57				
30	120	20	82.6	1.62	1.63	0.062	0.099	35.8
30	120	35	144.6	1.34				
30	120	35	144.6	1.08				
30	120	35	144.6	0.83				
30	120	35	144.6	1.15	1.10	0.214	0.340	56.7
30	120	50	206.6	1.33				
30	120	50	206.6	1.13				
30	120	50	206.6	1.07				
30	120	50	206.6	0.72	1.06	0.254	0.404	58.4
30	120	80	330.6	1.16				
30	120	80	330.6	1.31				
30	120	80	330.6	0.84				
30	120	80	330.6	0.58	0.97	0.327	0.521	61.8

Table B7. Ferrous chloride waste solution additions to digester 3, cone sludge

Date of Experiment: April 20 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	4.83				
30	120	0	0.0	4.37				
30	120	0	0.0	4.48				
30	120	0	0.0	4.29	4.49	0.237	0.376	0
30	120	3.5	10.7	2.50				
30	120	3.5	10.7	2.59				
30	120	3.5	10.7	2.72	2.60	0.109	0.272	42.1
30	120	6	18.4	1.53				
30	120	6	18.4	1.54				
30	120	6	18.4	1.65				
30	120	6	18.4	1.16	1.47	0.215	0.342	67.3
30	120	8	24.5	1.29				
30	120	8	24.5	1.17				
30	120	8	24.5	0.79				
30	120	8	24.5	1.41	1.16	0.268	0.426	74.1
30	120	13	39.8	0.64				
30	120	13	39.8	0.96				
30	120	13	39.8	0.69				
30	120	13	39.8	0.90	0.80	0.159	0.252	82.3

Table B8. Ferrous chloride reagent grade additions to digester 3, cone sludge

Date of Experiment: April 22 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2 4H_20$ (5g/L) (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	5.60				
30	120	0	0.0	5.24				
30	120	0	0.0	6.07				
30	120	0	0.0	5.84	5.69	0.353	0.561	0
30	120	4	11.2	2.37				
30	120	4	11.2	3.56				
30	120	4	11.2	2.82				
30	120	4	11.2	2.53	2.82	0.529	0.840	50.4
30	120	7	19.7	1.87				
30	120	7	19.7	1.65				
30	120	7	19.7	2.56				
30	120	7	19.7	1.56	1.91	0.456	0.725	66.5
30	120	11	30.9	1.04				
30	120	11	30.9	0.63				
30	120	11	30.9	0.68				
30	120	11	30.9	1.18	0.88	0.268	0.426	84.5
30	120	16	44.9	0.80				
30	120	16	44.9	0.35				
30	120	16	44.9	0.77				
30	120	16	44.9	0.80	0.68	0.221	0.352	88.1

Table B9. Ferrous chloride reagent grade additions to digester 6, cone sludge

Date of Experiment: April 30 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2\ 4H_2O$ 5g/L (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average % Reduction
30	120	0	0	4.72				
30	120	0	0	4.41				
30	120	0	0	4.99				
30	120	0	0	4.94	4.76	0.263	0.419	0
30	120	4	11.2	2.10				
30	120	4	11.2	2.28				
30	120	4	11.2	2.21				
30	120	4	11.2	2.26	2.21	0.080	0.127	53.5
30	120	7	19.7	1.16				
30	120	7	19.7	1.45				
30	120	7	19.7	2.06				
30	120	7	19.7	1.14	1.45	0.428	0.680	69.6
30	120	11	30.9	0.74				
30	120	11	30.9	0.71				
30	120	11	30.9	0.65				
30	120	11	30.9	0.94	0.76	0.126	0.200	84.0
30	120	16	44.9	0.56				
30	120	16	44.9	0.71				
30	120	16	44.9	0.74				
30	120	16	44.9	0.79	0.70	0.102	0.162	85.3

Table B10. Ferrous chloride waste solution additions to digester 6, cone sludge

Date of Experiment: May 1 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0	5.16				
30	120	0	0	5.10				
30	120	0	0	5.91				
30	120	0	0	5.78	5.49	0.417	0.663	0
30	120	4	12.24	2.55				
30	120	4	12.24	2.40				
30	120	4	12.24	3.59				
30	120	4	12.24	3.85	3.10	0.729	1.160	43.6
30	120	8	24.48	1.58				
30	120	8	24.48	1.44				
30	120	8	24.48	2.40				
30	120	8	24.48	1.83	1.81	0.422	0.671	67.0
30	120	12	36.72	1.06				
30	120	12	36.72	1.03				
30	120	12	36.72	0.82				
30	120	12	36.72	0.94	0.96	0.110	0.174	82.5
30	120	17	52.02	0.73				
30	120	17	52.02	0.98				
30	120	17	52.02	0.92				
30	120	17	52.02	1.09	0.93	0.151	0.240	83.1

Table B11. Ferrous chloride reagent grade additions to digester 6, cone sludge

Date of Experiment: May 7 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ $4H_2O$ 5g/L (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0	7.75				
30	120	0	0	8.40				
30	120	0	0	7.61				
30	120	0	0	8.09	7.96	0.353	0.561	0
30	120	6	16.9	3.08				
30	120	6	16.9	4.61				
30	120	6	16.9	3.81				
30	120	6	16.9	4.23	3.93	0.66	1.044	50.7
30	120	8	22.5	2.54				
30	120	8	22.5	2.88				
30	120	8	22.5	2.30				
30	120	8	22.5	3.15	2.72	0.374	0.594	65.9
30	120	12	33.7	1.67				
30	120	12	33.7	1.53				
30	120	12	33.7	1.92				
30	120	12	33.7	1.72	1.71	0.164	0.261	78.5
30	120	18	50.6	1.30				
30	120	18	50.6	0.79				
30	120	18	50.6	1.18				
30	120	18	50.6	1.26	1.13	0.235	0.373	85.8

Table B12. Ferrous chloride waste solution additions to digester 3, cone sludge

Date of Experiment: May 8 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	7.63				
30	120	0	0.0	8.30	7.96	0.472	4.238	0
30	120	6	18.4	3.35				
30	120	6	18.4	4.81				
30	120	6	18.4	4.46				
30	120	6	18.4	4.04	4.16	0.628	0.998	47.7
30	120	8	24.5	2.68				
30	120	8	24.5	3.37				
30	120	8	24.5	2.93				
30	120	8	24.5	2.17	2.79	0.501	0.796	65.0
30	120	12	36.7	1.82				
30	120	12	36.7	1.63				
30	120	12	36.7	2.02				
30	120	12	36.7	1.92	1.85	0.169	0.269	76.8
30	120	20	61.2	0.92				
30	120	20	61.2	1.31				
30	120	20	61.2	1.13				
30	120	20	61.2	1.16	1.13	0.161	0.256	85.8

Table B13. Ferric chloride reagent grade additions to digester 6, cone sludge

Date of Experiment: May 12 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_3$ $6H_2O$ 10 g/L (mL)	As Fe^{3+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0	7.61				
30	120	0	0	8.40				
30	120	0	0	8.32				
30	120	0	0	7.75	8.02	0.400	0.636	0
30	120	12	50	1.96				
30	120	12	50	1.68				
30	120	12	50	3.00	2.21	0.695	1.730	72.4
30	120	25	103	1.86				
30	120	25	103	1.65				
30	120	25	103	1.34				
30	120	25	103	1.17	1.50	0.310	0.492	81.3
30	120	40	165	1.69				
30	120	40	165	1.53				
30	120	40	165	1.17				
30	120	40	165	1.20	1.40	0.252	0.626	82.6
30	120	70	289	1.22				
30	120	70	289	0.85				
30	120	70	289	1.37	1.15	0.270	0.428	85.7

Table B14. Ferrous chloride reagent grade additions to digester 3, cone sludge

Date of Experiment: May 13 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2 4H_20$ (5g/L) (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	9.13				
30	120	0	0.0	8.41				
30	120	0	0.0	8.56				
30	120	0	0.0	8.72	8.70	0.311	0.495	0
30	120	7	19.7	3.14				
30	120	7	19.7	3.95				
30	120	7	19.7	3.49				
30	120	7	19.7	3.21	3.45	0.370	0.588	60.4
30	120	9	25.3	2.12				
30	120	9	25.3	3.02				
30	120	9	25.3	2.44	2.53	0.454	1.127	71.0
30	120	13	36.5	1.56				
30	120	13	36.5	1.58				
30	120	13	36.5	1.31				
30	120	13	36.5	1.74	1.55	0.179	0.284	82.3
30	120	20	56.2	0.89				
30	120	20	56.2	0.86				
30	120	20	56.2	0.99				
30	120	20	56.2	0.92	0.91	0.056	0.089	89.5

Table B15. Ferrous chloride waste solution additions to digester 6, cone sludge

Date of Experiment: May 15 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	As Fe^{2+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	8.49				
30	120	0	0.0	9.62				
30	120	0	0.0	9.29				
30	120	0	0.0	9.12	9.13	0.473	0.752	0
30	120	7	21.4	2.60				
30	120	7	21.4	3.64				
30	120	7	21.4	4.58				
30	120	7	21.4	4.23	3.76	0.866	1.377	58.8
30	120	10	30.6	1.90				
30	120	10	30.6	2.43				
30	120	10	30.6	2.66				
30	120	10	30.6	2.77	2.44	0.386	0.614	73.3
30	120	14	42.8	1.28				
30	120	14	42.8	1.57				
30	120	14	42.8	1.36				
30	120	14	42.8	1.95	1.54	0.300	0.477	83.1
30	120	20	61.2	1.20				
30	120	20	61.2	1.09				
30	120	20	61.2	1.28				
30	120	20	61.2	0.97	1.13	0.132	0.210	87.6

Table B16. Ferric chloride reagent grade additions to digester 3, cone sludge

Date of Experiment: May 18 1998

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_3 6H_20$ (10g/L) (mL)	As Fe^{3+} (mg/L)	Sulfide Titrated (mg / 0.5L)	Mean (mg / 0.5L)	Standard Deviation	Error for 95% confidence	Average Percent Reduction (%)
30	120	0	0.0	5.37				
30	120	0	0.0	5.27				
30	120	0	0.0	5.67				
30	120	0	0.0	5.68	5.50	0.209	0.333	0
30	120	12	49.6	2.06				
30	120	12	49.6	2.63				
30	120	12	49.6	2.61				
30	120	12	49.6	2.73	2.51	0.302	0.480	54.4
30	120	25	103.3	2.04				
30	120	25	103.3	1.77				
30	120	25	103.3	1.60				
30	120	25	103.3	1.92	1.83	0.193	0.307	66.7
30	120	40	165.3	1.83				
30	120	40	165.3	1.73				
30	120	40	165.3	1.28				
30	120	40	165.3	1.79	1.66	0.258	0.409	69.9
30	120	70	289.3	1.41				
30	120	70	289.3	1.22				
30	120	70	289.3	1.43				
30	120	70	289.3	1.37	1.36	0.097	0.155	75.3

APPENDIX C. % Reduction Versus Chemical Dose Curves (All Iron Doses Added to 0.5L of Sludge)

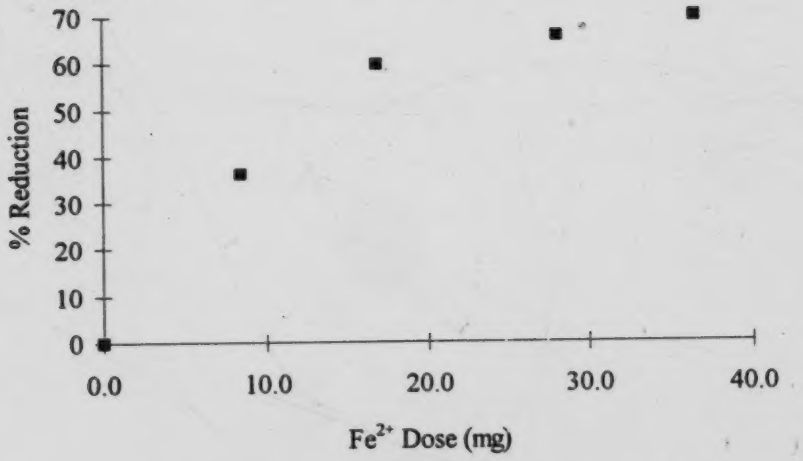

Figure C1. % Reduction vs. Fe^{2+} Dose, Digester 6, 7.9 m, Digester sulfide mass = 1.79 mg (blank).

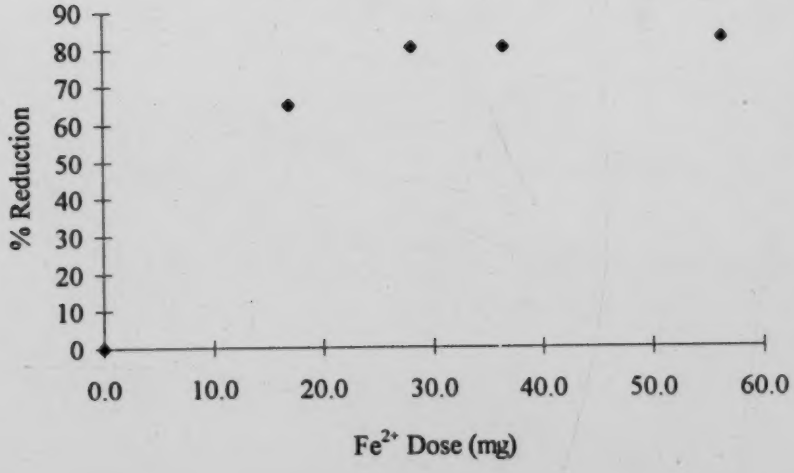

Figure C2. % Reduction vs. Fe^{2+} Dose, Digester 6, 7.9 m, Digester sulfide mass = 3.64 mg (blank).

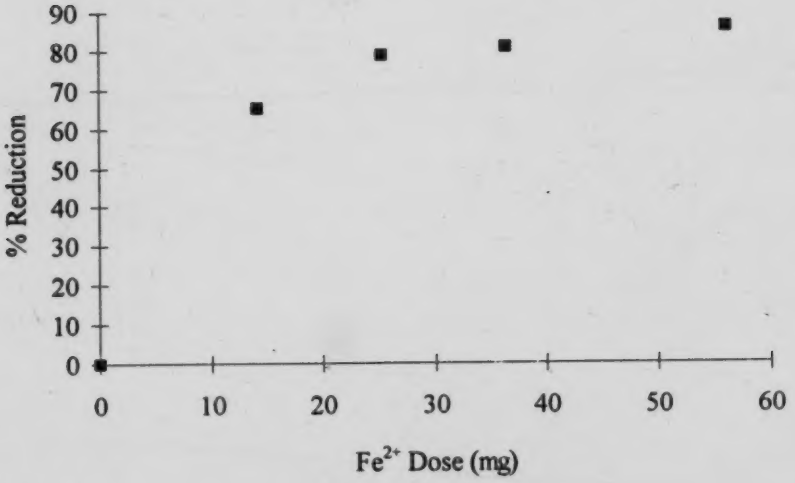

Figure C3. % Reduction vs. Fe^{2+} Dose, Digester 6, 7.9 m
Digester sulfide mass = 5.01 mg (blank).

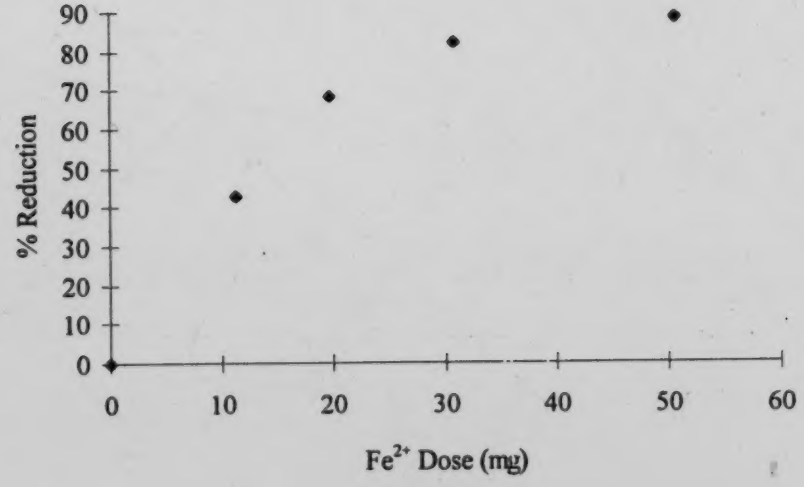

Figure C4. % Reduction vs. Fe^{2+} Dose, Digester 6, 7.9 m
Digester sulfide mass = 6.27 mg (blank).

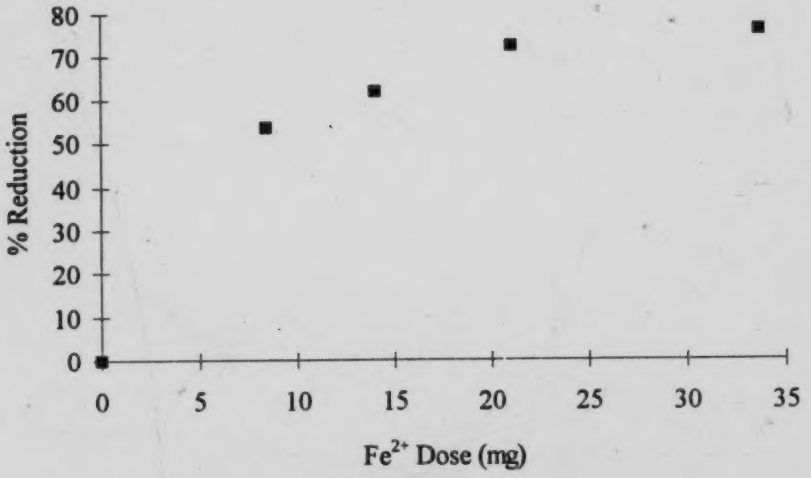

Figure C5. % Reduction vs. Fe^{2+} Dose, Digester 3, 7.9 m
Digester sulfide mass = 2.70 mg (blank).

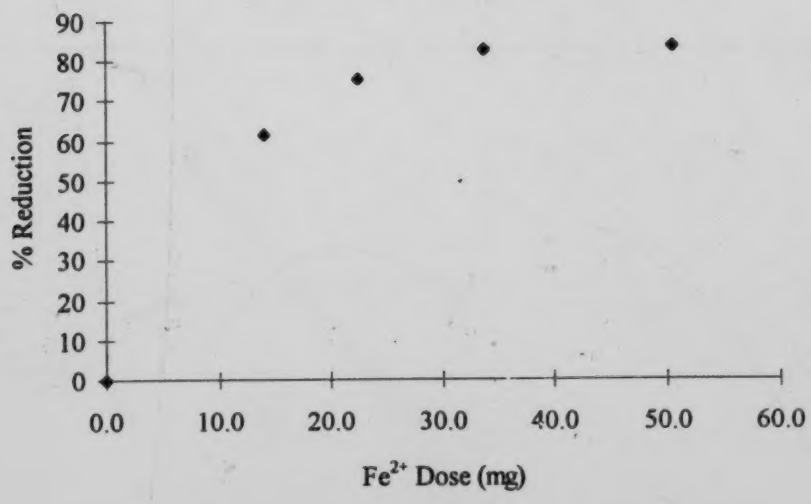

Figure C6. % Reduction vs. Fe^{2+} Dose, Digester 3, 7.9 m
Digester sulfide mass = 4.44 mg (blank).

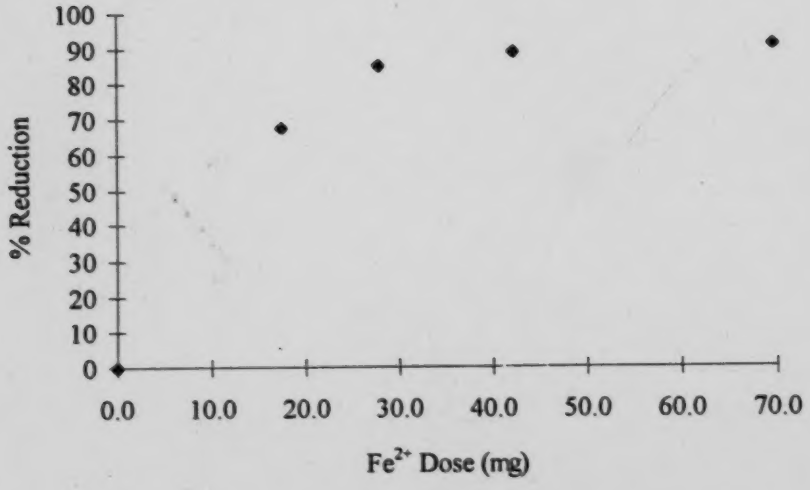

Figure C7. % Reduction vs. Fe^{2+} Dose, Digester 3, 7.9 m
Digester sulfide mass = 6.15 mg (blank).

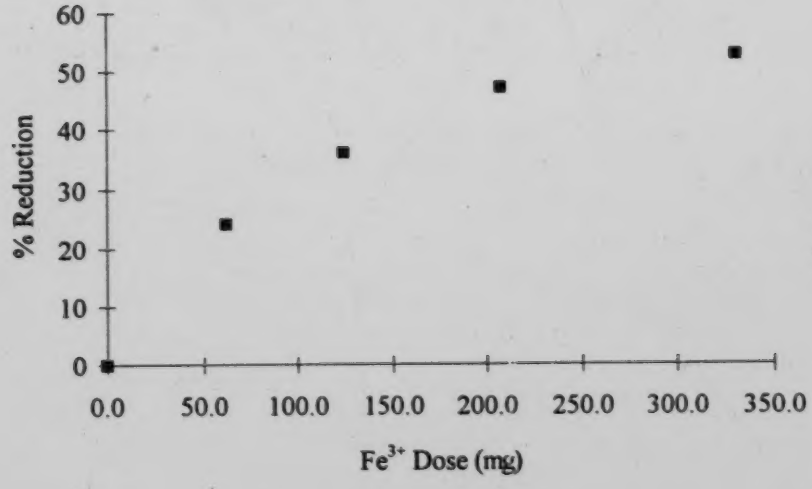

Figure C8. % Reduction vs. Fe^{3+} Dose, Digester 6, 7.9 m
Digester sulfide mass = 1.75 mg (blank).

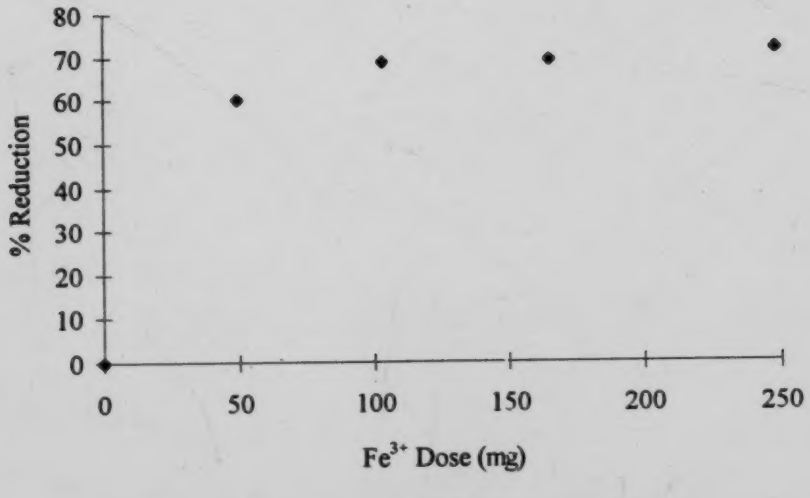

Figure C9. % Reduction vs. Fe^{3+} Dose, Digester 6, 7.9 m
Digester sulfide mass = 5.32 mg (blank).

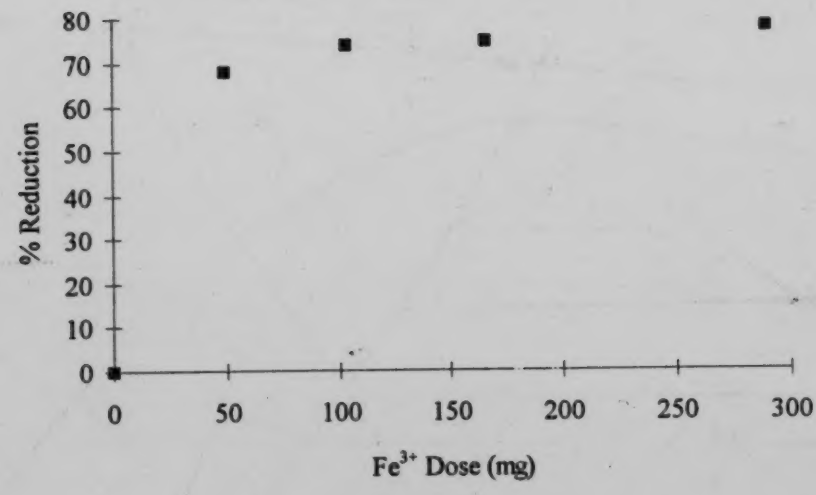

Figure C10. % Reduction vs. Fe^{3+} Dose, Digester 6, 7.9 m
Digester sulfide mass = 7.41 mg (blank).

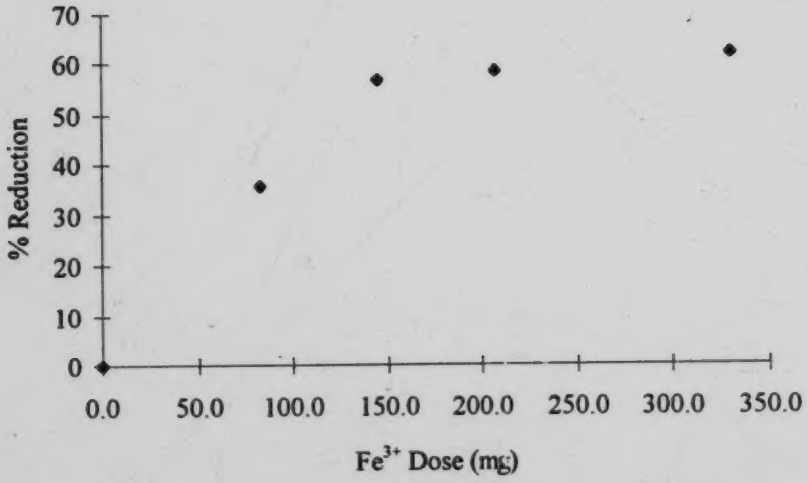

Figure C11. % Reduction vs. Fe^{3+} Dose, Digester 6, Cone Digester sulfide mass = 2.54 mg (blank).

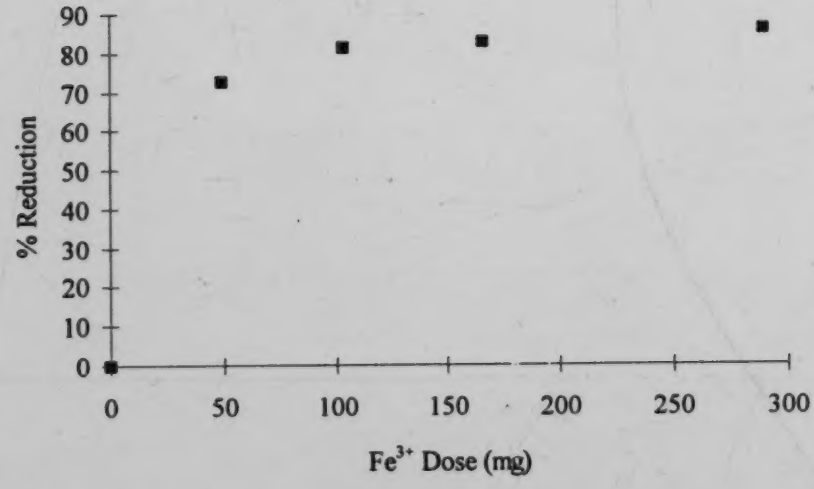

Figure C12. % Reduction vs. Fe^{3+} Dose, Digester 6, Cone Digester sulfide mass = 8.02 mg (blank).

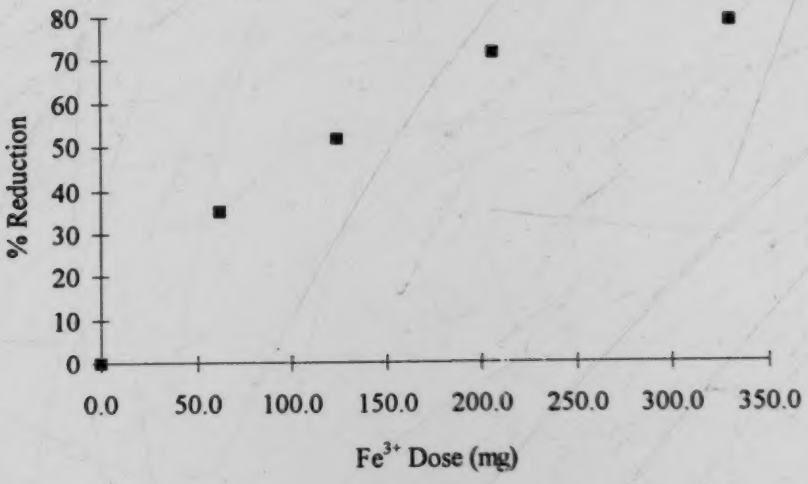

Figure C13. % Reduction vs. Fe^{3+} Dose, Digester 3, Cone
Digester sulfide mass = 2.08 mg (blank).

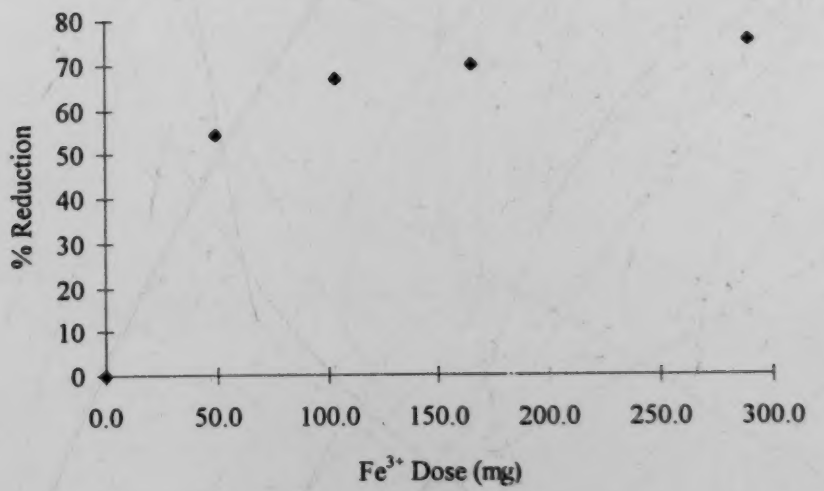

Figure C14. % Reduction vs. Fe^{3+} Dose, Digester 3, Cone
Digester sulfide mass = 5.50 mg (blank).

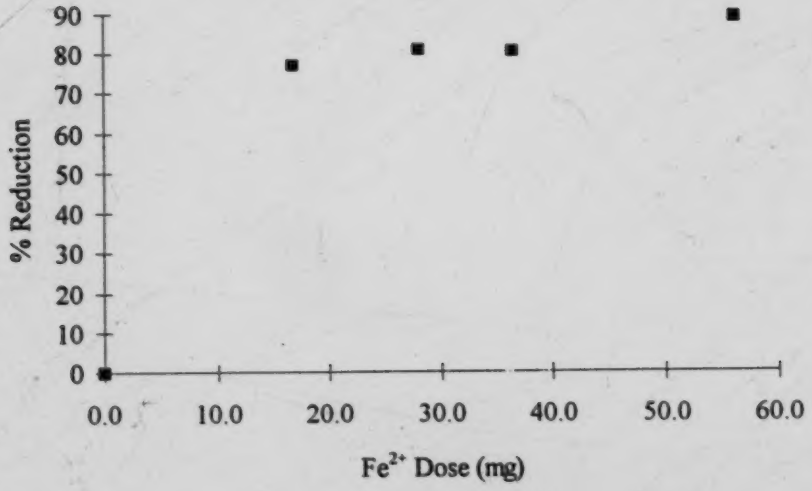

Figure C15. % Reduction vs. Fe^{2+} Dose, Digester 6, Cone Digester sulfide mass = 3.06 mg (blank).

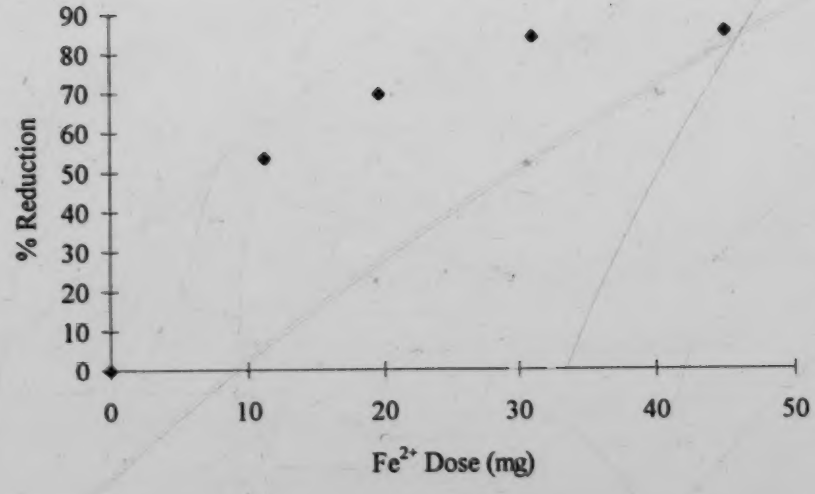

Figure C16. % Reduction vs. Fe^{2+} Dose, Digester 6, Cone Digester sulfide mass = 4.76 mg (blank).

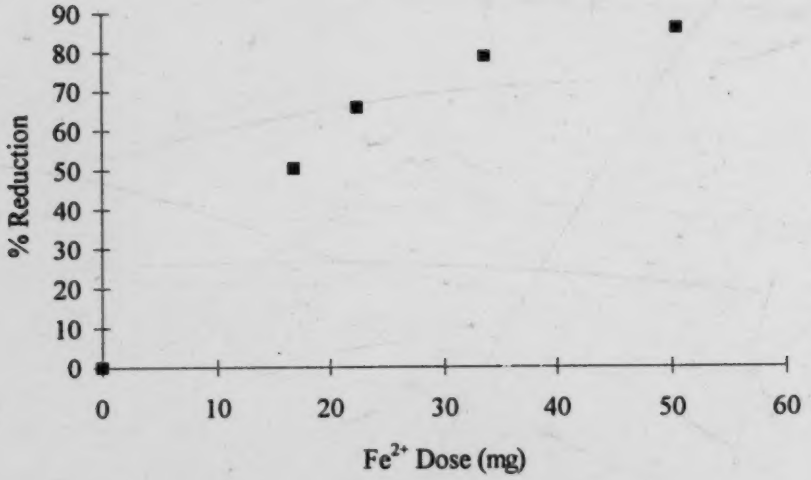

Figure C17. % Reduction vs. Fe^{2+} Dose, Digester 6, Cone
Digester sulfide mass = 7.96 mg (blank).

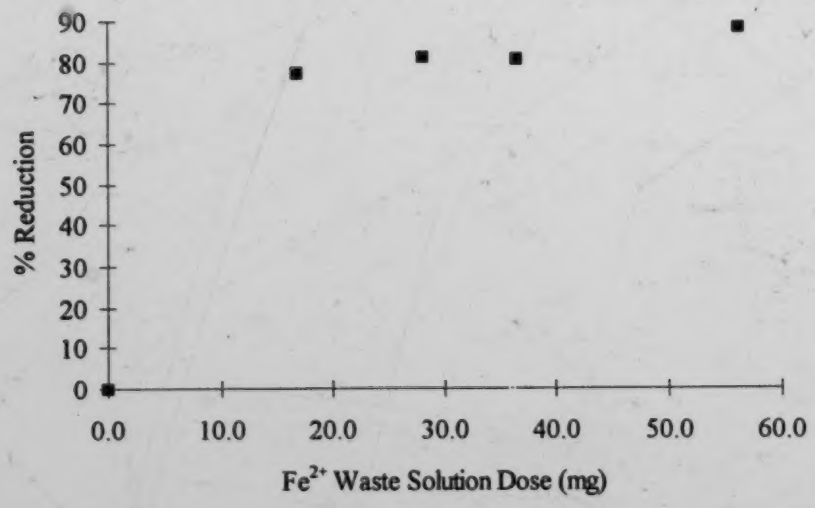

Figure C18. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 3, 7.9 m
Digester sulfide mass = 2.68 mg (blank).

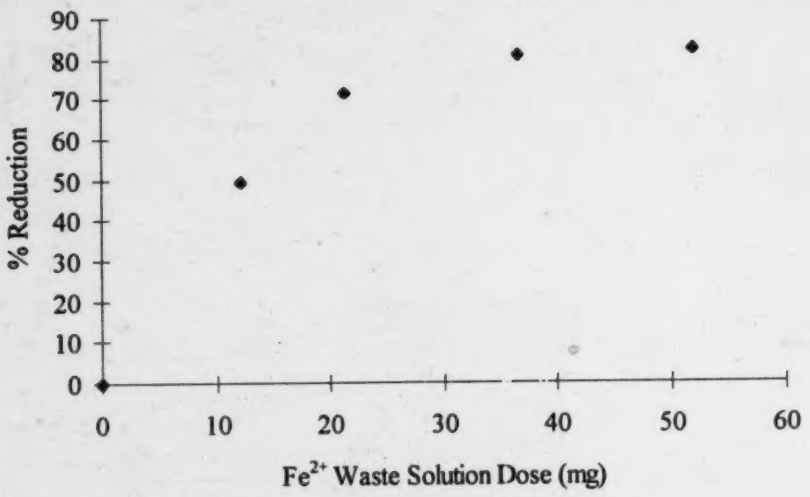

Figure C19. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 3, 7.9 m Digester sulfide mass = 4.46 mg (blank).

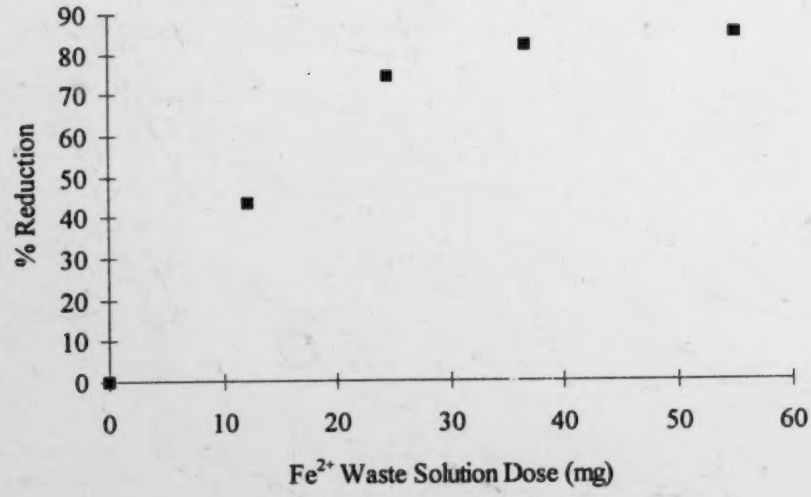

Figure C20. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 3, 7.9 m Digester sulfide mass = 6.81 mg (blank).

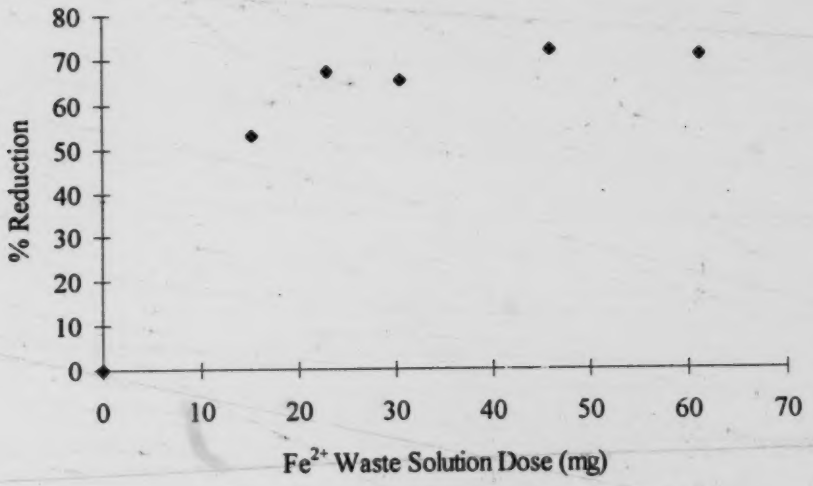

Figure C21. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 6, 7.9 m Digester sulfide mass = 1.77 mg (blank).

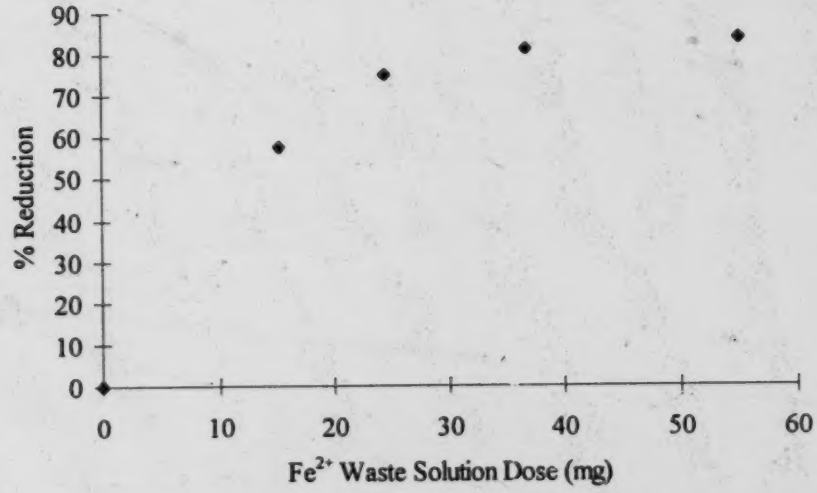

Figure C22. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 6, 7.9 m Digester sulfide mass = 4.68 mg (blank).

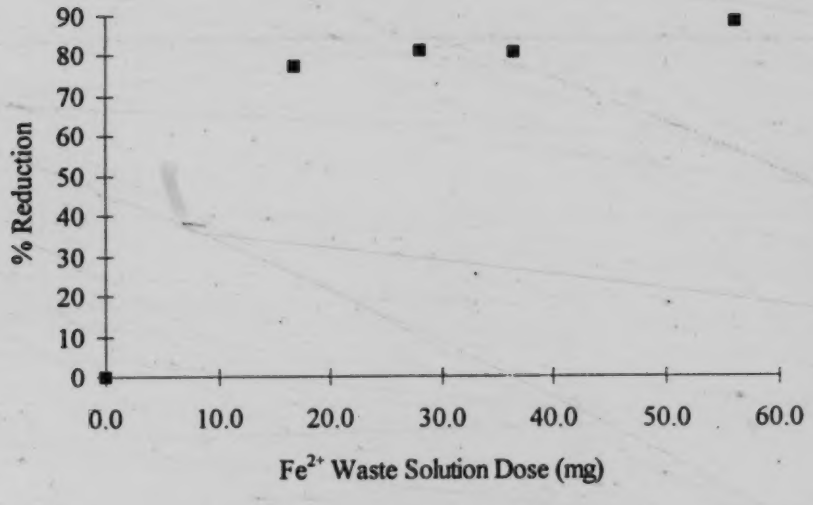

Figure C23. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 6, 7.9 m Digester sulfide mass = 5.44 mg (blank).

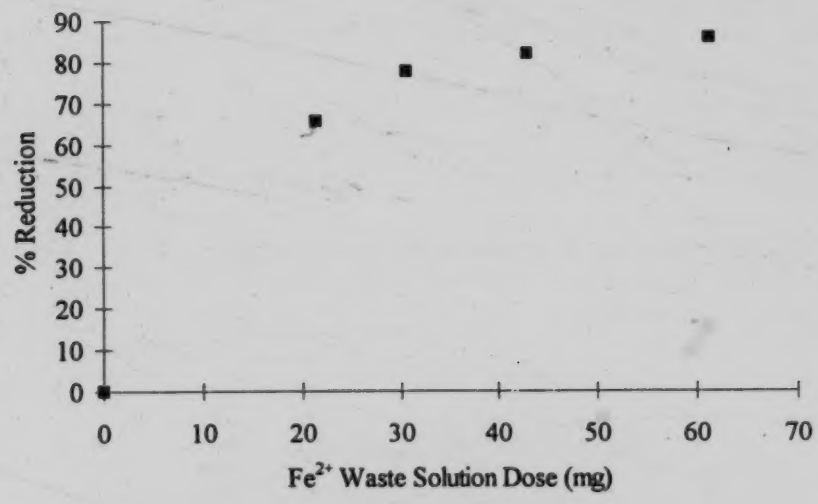

Figure C24. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 6, 7.9 m Digester sulfide mass = 6.04 mg (blank).

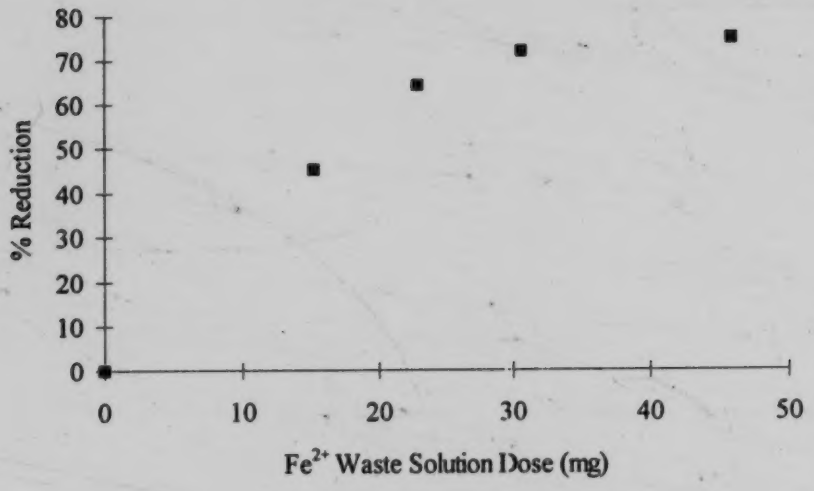

Figure C25. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 3, Cone Digester sulfide mass = 2.03 mg (blank).

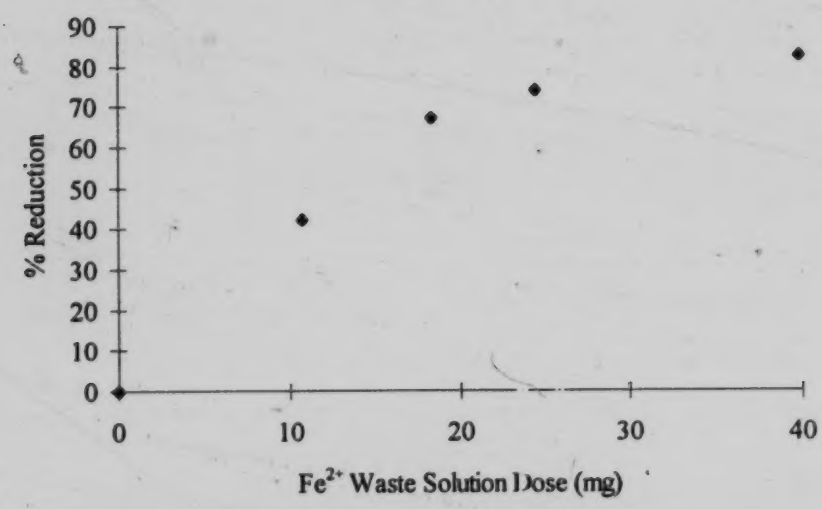

Figure C26. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 3, Cone Digester sulfide mass = 4.49 mg (blank).

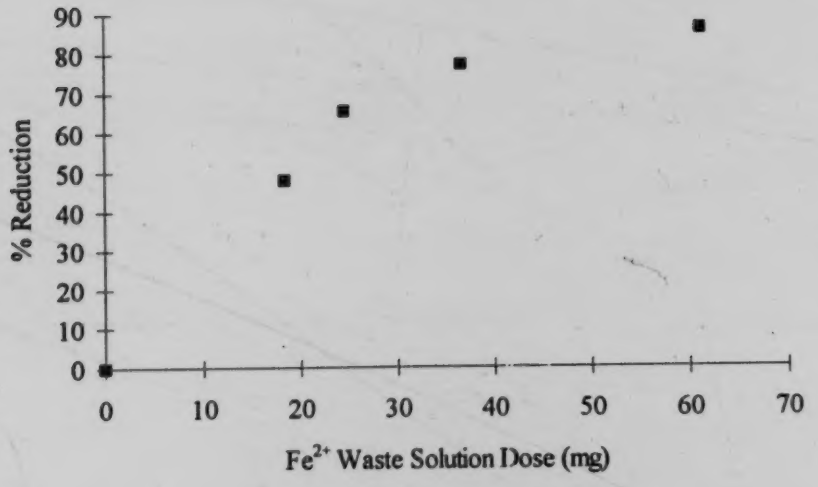

Figure C27. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 3, Cone Digester sulfide mass = 7.96 mg (blank).

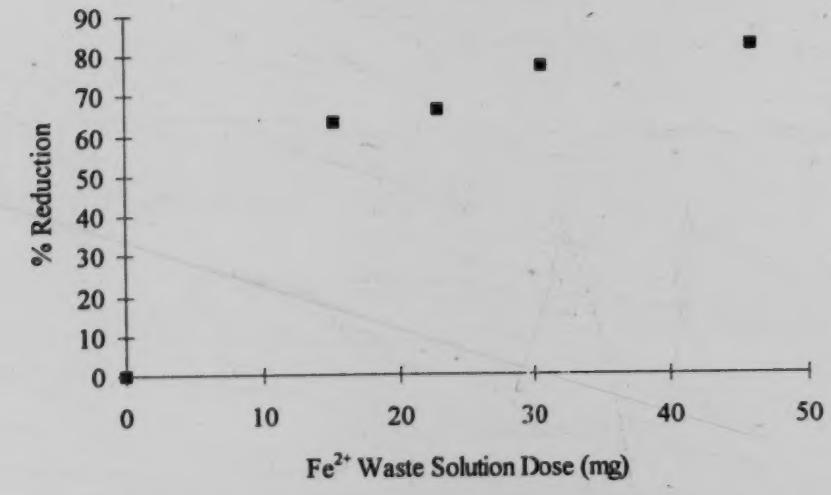

Figure C28. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 6, Cone Digester sulfide mass = 3.15 mg (blank).

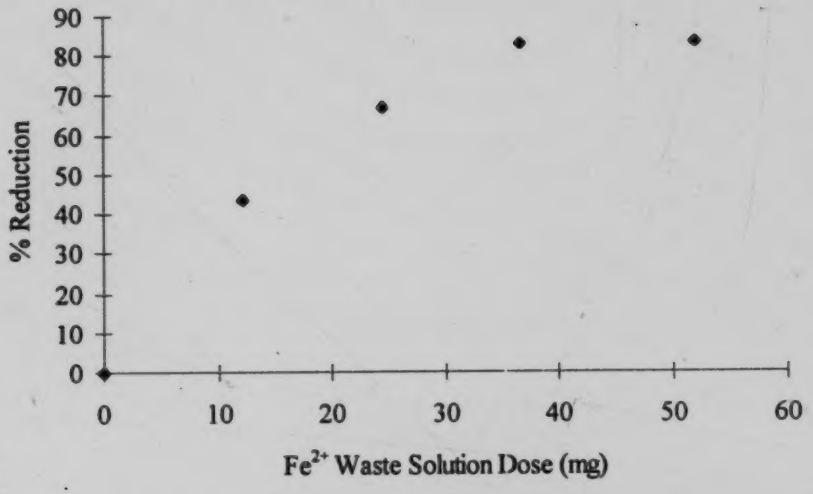

Figure C29. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 6, Cone Digester sulfide mass = 5.49 mg (blank).

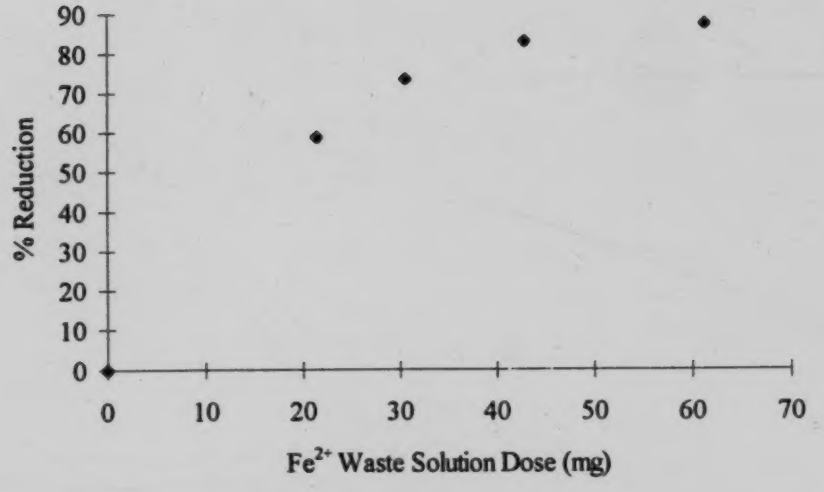

Figure C30. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 6, Cone Digester sulfide mass = 9.13 mg (blank).

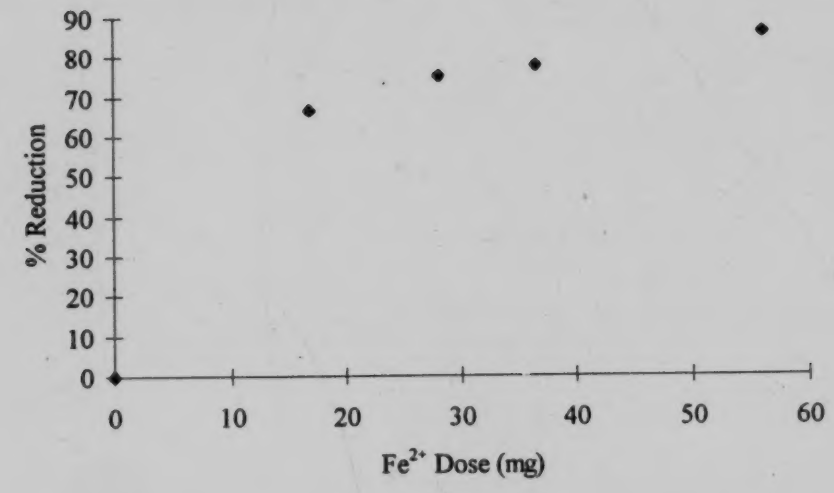

Figure C31. % Reduction vs. Fe^{2+} Waste Solution Dose, Digester 3, Cone
Digester sulfide mass = 2.48 mg (blank).

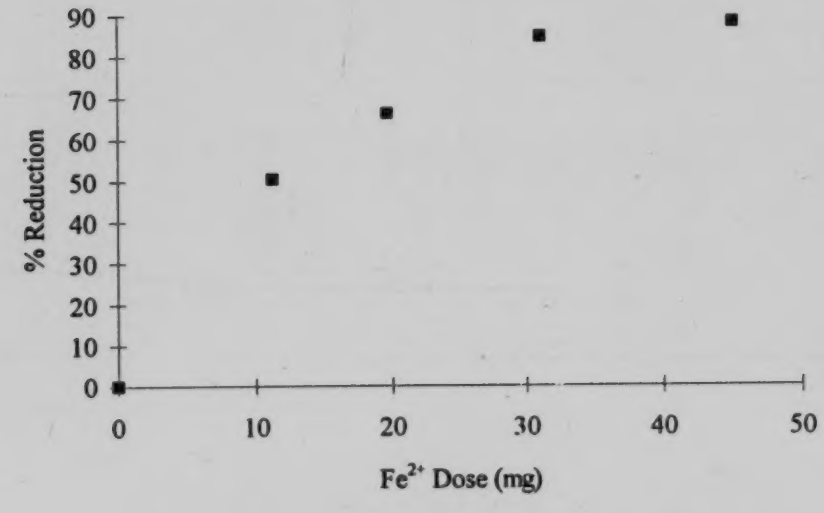

Figure C32. % Reduction vs. Fe^{2+} Dose, Digester 3, Cone
Digester sulfide mass = 5.69 mg (blank).

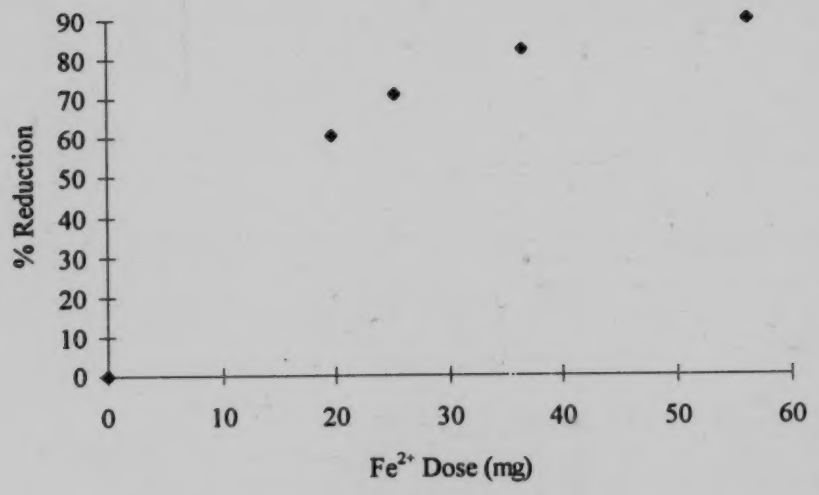

Figure C33. % Reduction vs. Fe^{2+} Dose, Digester 3, Cone
Digester sulfide mass = 8.70 mg (blank).

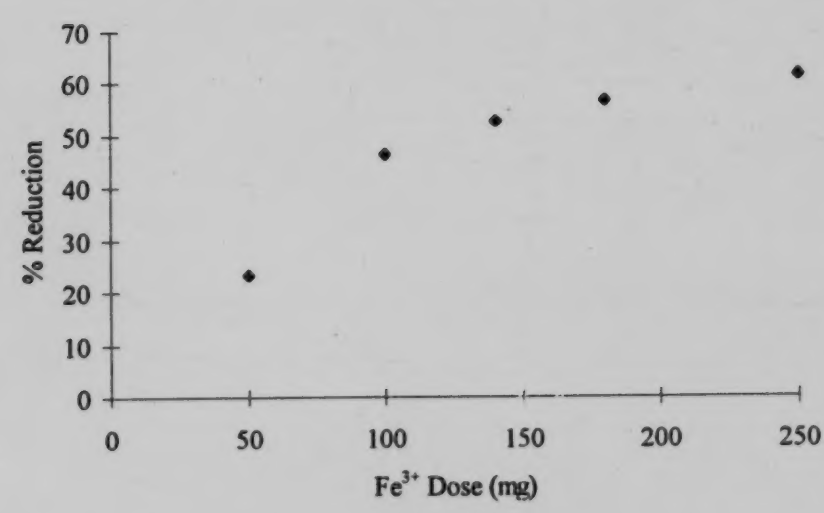

Figure C34. % Reduction vs. Fe^{3+} Dose, Digester 3, 7.9 m
Digester sulfide mass = 1.87 mg (blank).

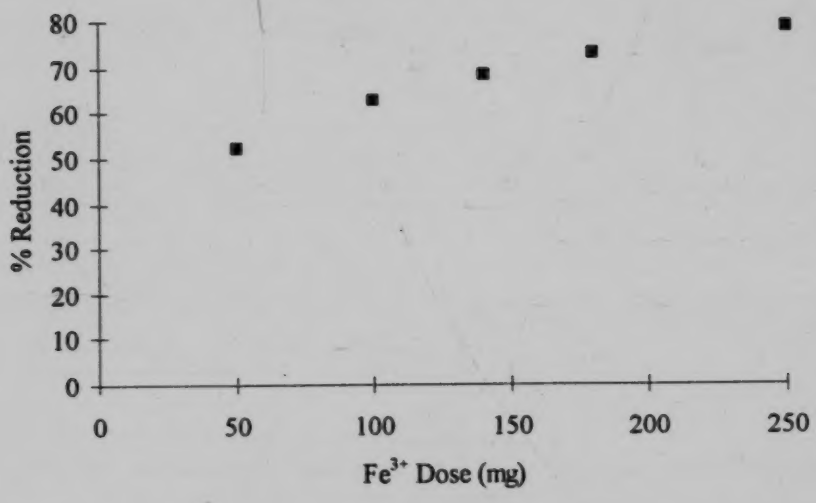

Figure C35. % Reduction vs. Fe^{3+} Dose, Digester 3, 7.9 m
Digester sulfide mass = 5.71 mg (blank).

APPENDIX D. Percent Reduction Contours

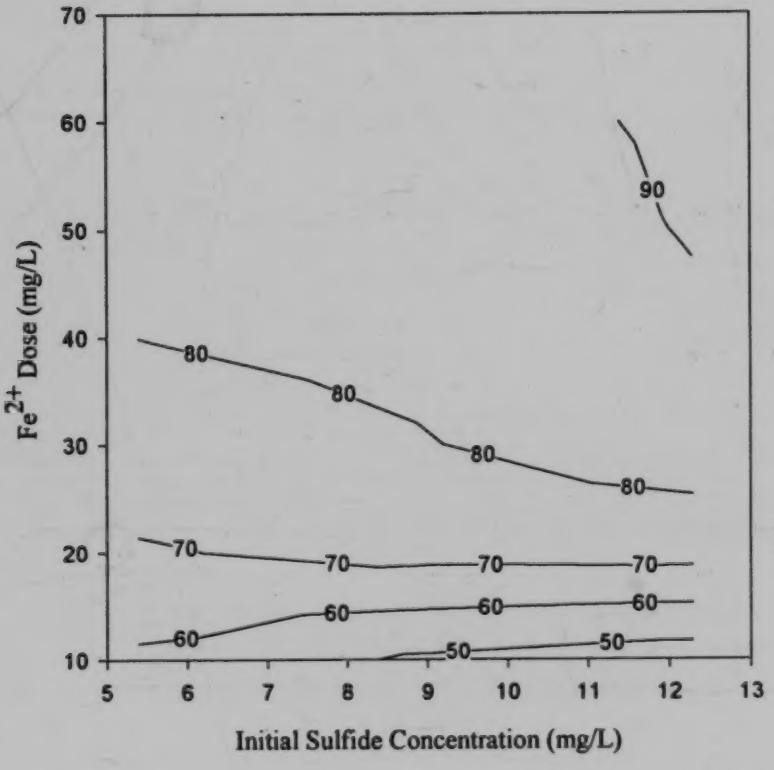

Figure D1. % Reduction Contours (Digester 3, 7.9 m, Fe^{2+} Reagent Grade).

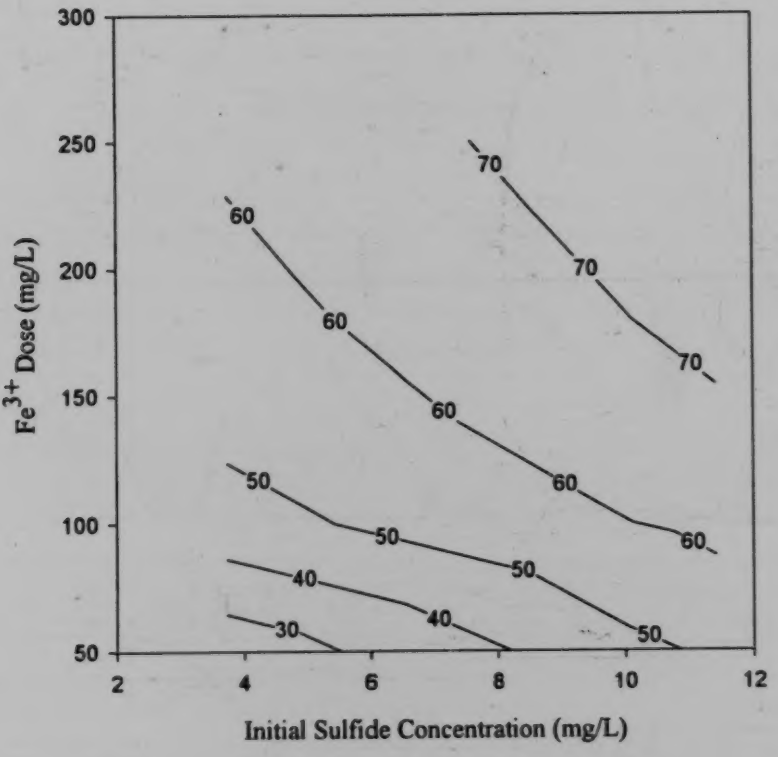

Figure D2. % Reduction Contours (Digester 3, 7.9 m, Fe^{3+} Reagent Grade).

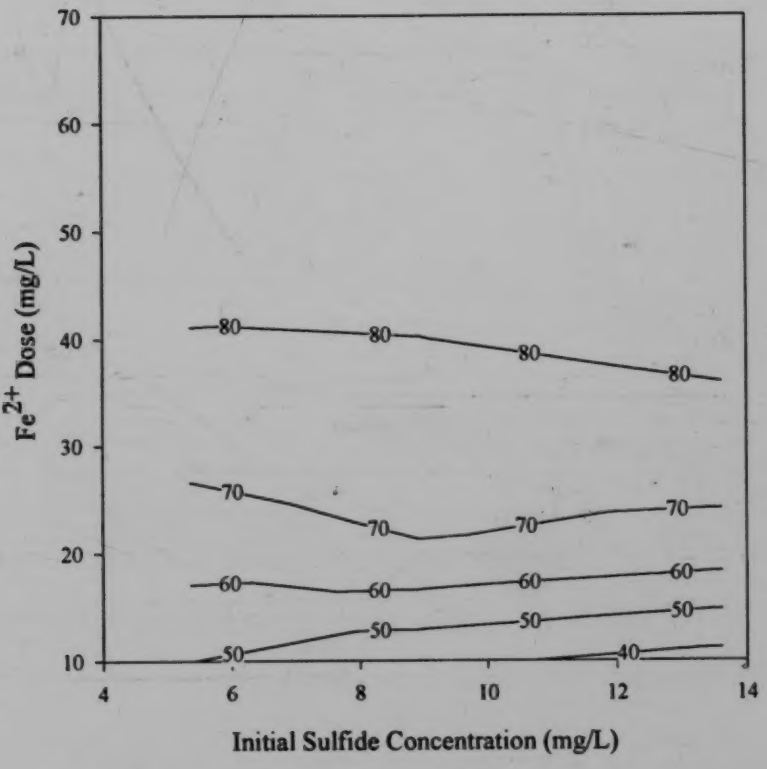

Figure D3. % Reduction Contours (Digester 3, 7.9 m, Fe^{2+} Waste Solution).

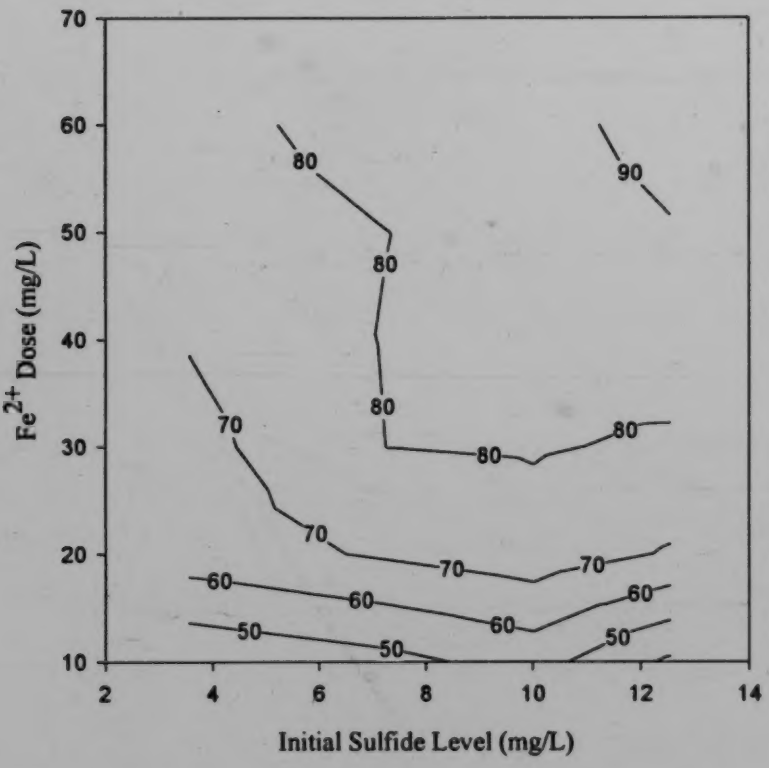

Figure D4. % Reduction Contours (Digester 6, 7.9 m, Fe^{2+} Reagent Grade).

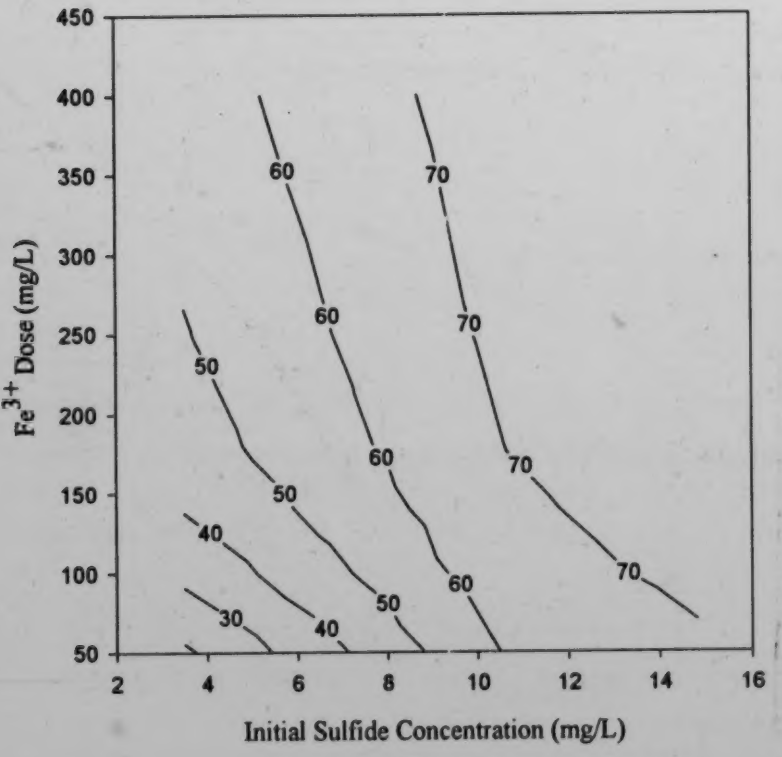

Figure D5. % Reduction Contours (Digester 6, 7.9 m, Fe^{3+} Reagent Grade).

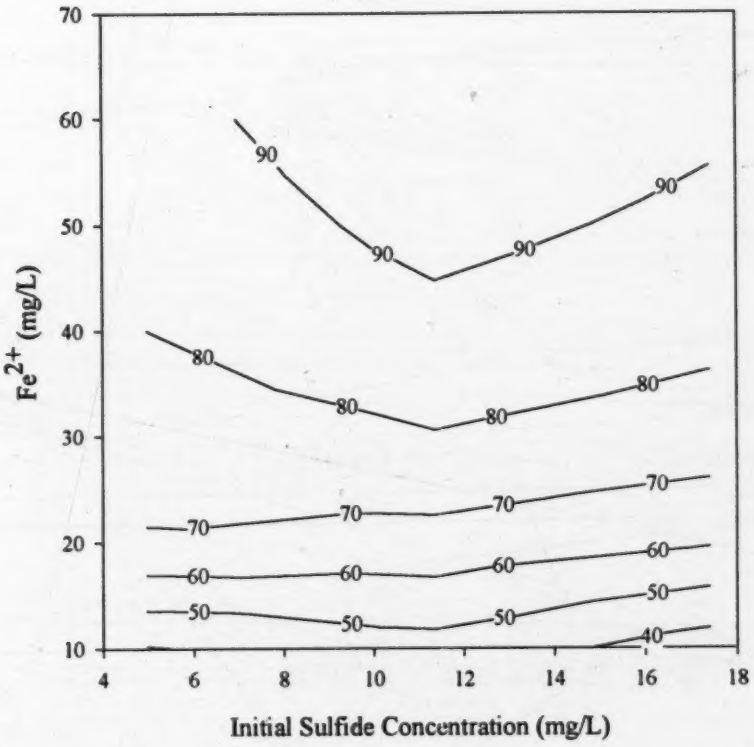

Figure D6. % Reduction Contours (Digester 6, 7.9 m, Fe^{2+} Waste Solution).

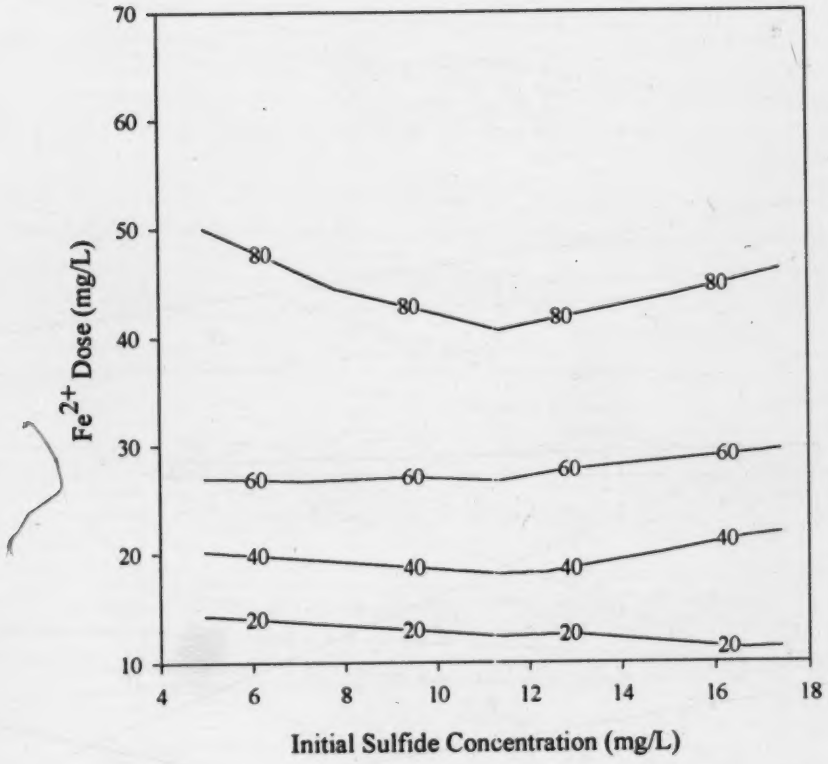

Figure D7. % Reduction Contours (Digester 3, Cone Level, Fe^{2+} Reagent Grade).

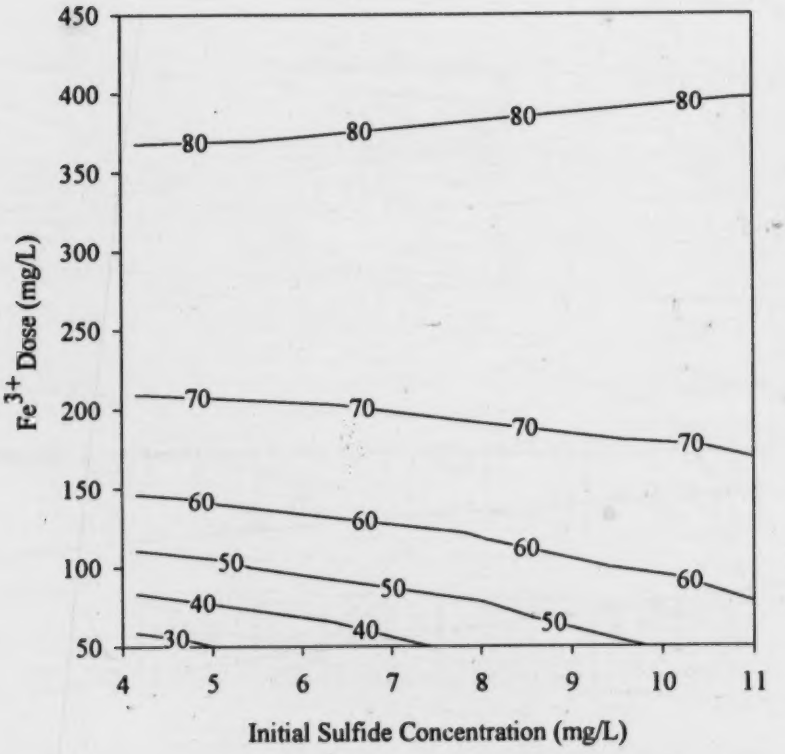

Figure D8. % Reduction Contours (Digester 3, Cone Level, Fe^{3+} Reagent Grade).

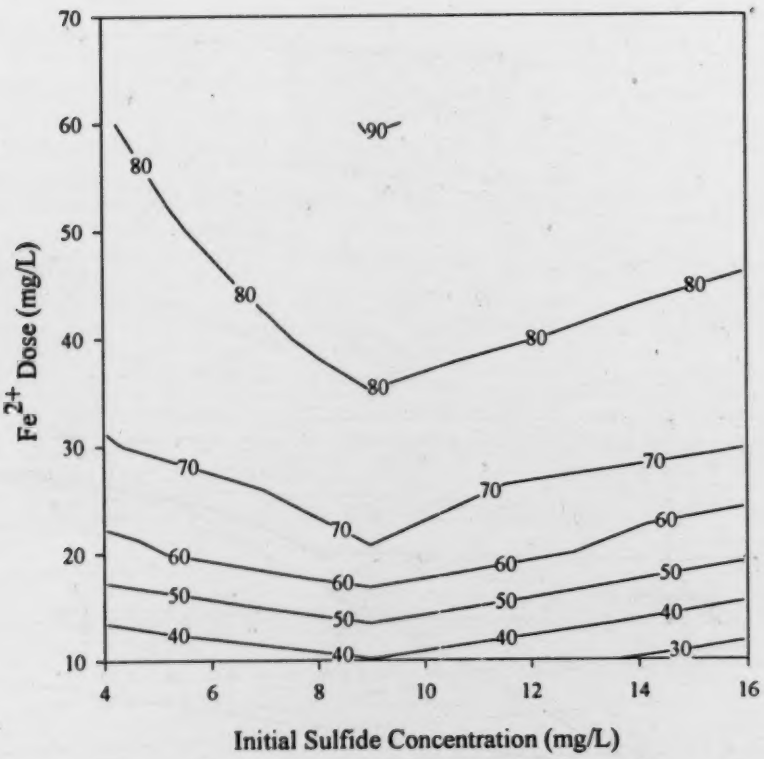

Figure D9. % Reduction Contours (Digester 3, Cone Level, Fe^{2+} Waste Solution).

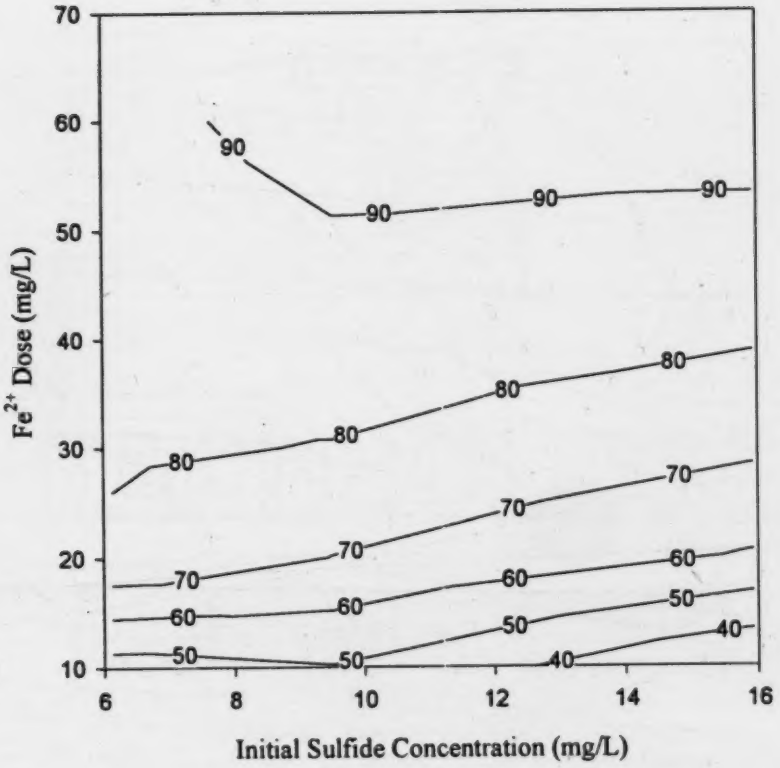

Figure D10. % Reduction Contours (Digester 6, Cone Level, Fe^{2+} Reagent Grade).

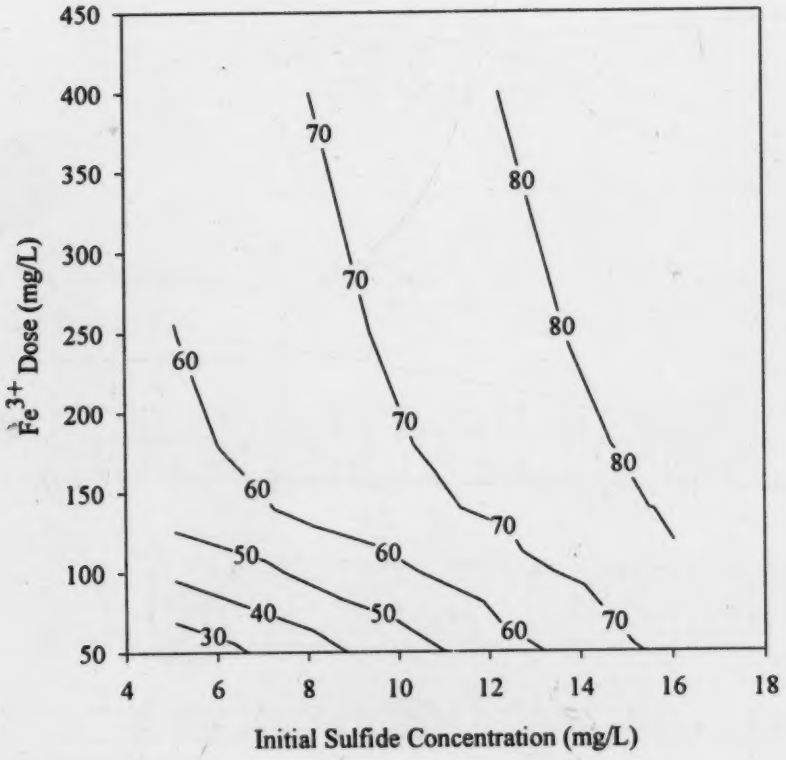

Figure D11. % Reduction Contours (Digester 6, Cone Level, Fe^{3+} Reagent Grade).

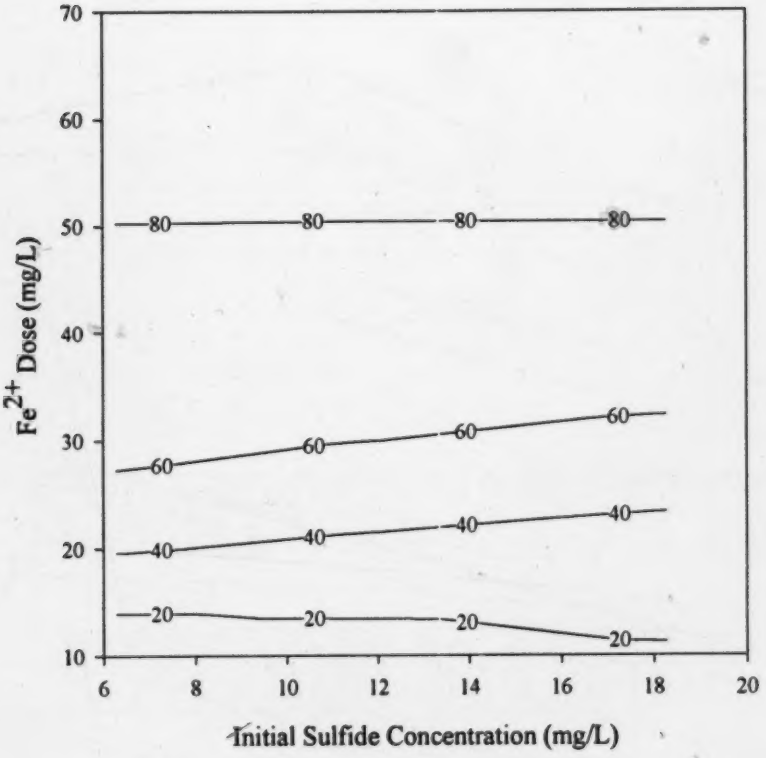

Figure D12. % Reduction Contours (Digester 6, Cone Level, Fe^{2+} Waste Solution).

APPENDIX E. Sulfide Titrated Versus Sparge Time Curves

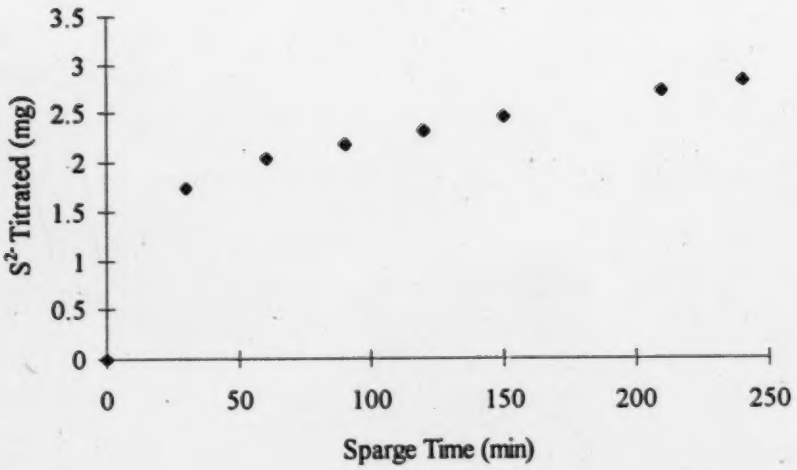

Figure E1. Sulfide Titrated vs. Sparge Time (Digester 3, 7.9 m, March 19 1998).

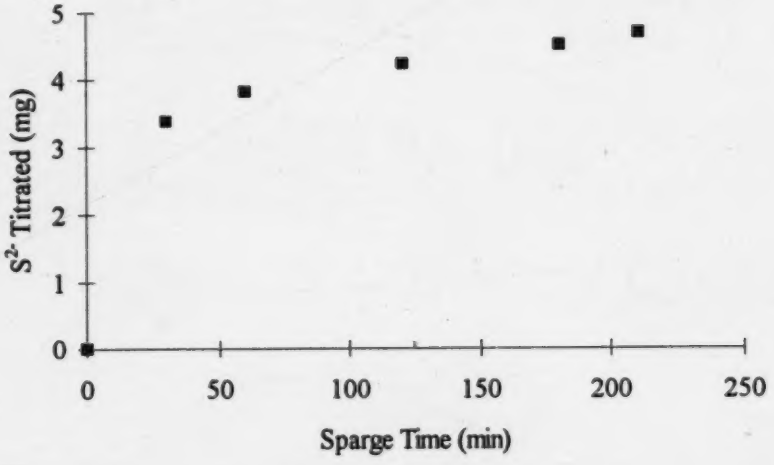

Figure E2. Sulfide Titrated vs. Sparge Time (Digester 3, 7.9 m, April 17 1998).

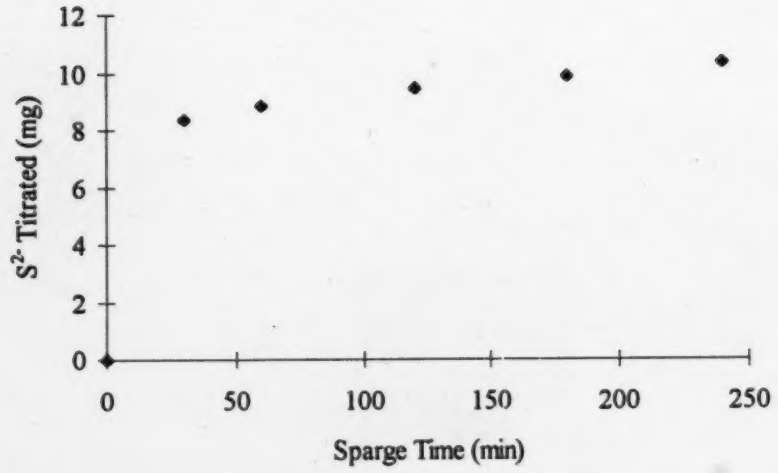

Figure E3. Sulfide Titrated vs. Sparge Time (Digester 3, 7.9 m, May 14 1998).

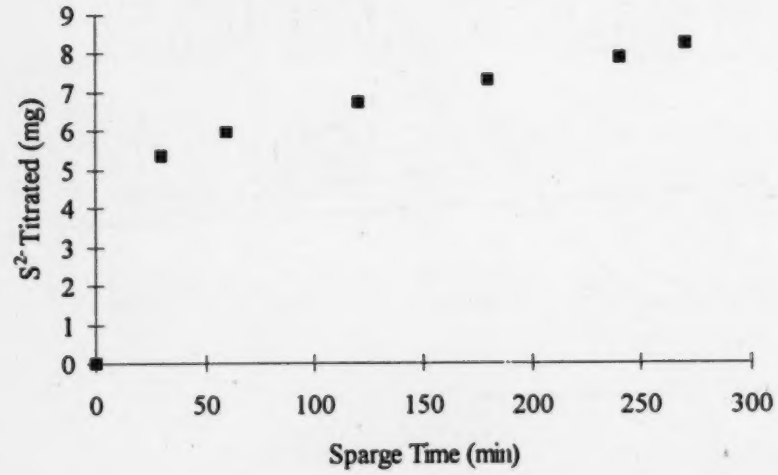

Figure E4. Sulfide Titrated vs. Sparge Time (Digester 3, 7.9 m, May 20 1998).

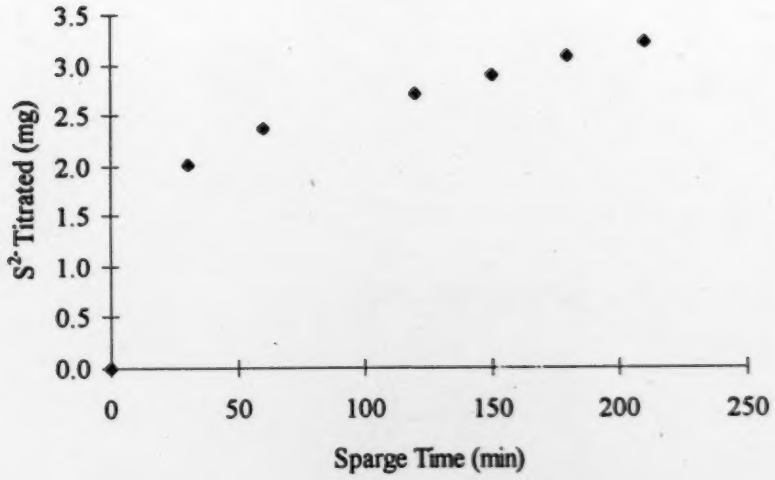

Figure E5. Sulfide Titrated vs. Sparge Time (Digester 5, 7.9 m, March 31 1998).

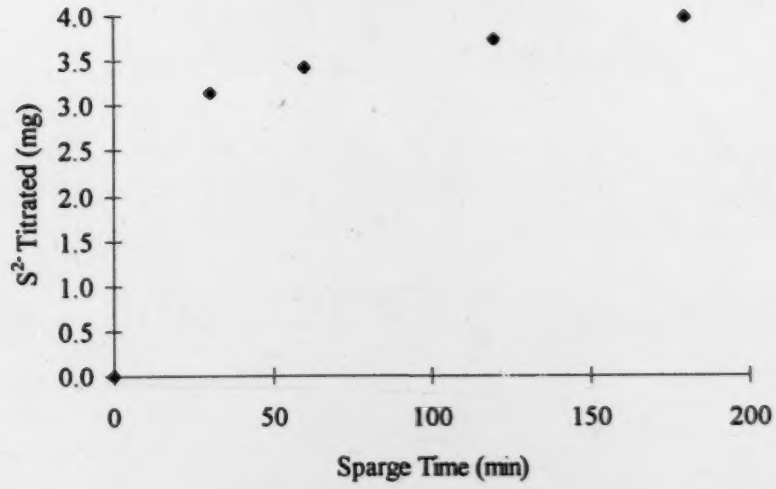

Figure E6. Sulfide Titrated vs. Sparge Time (Digester 5, Cone Level, April 2 1998).

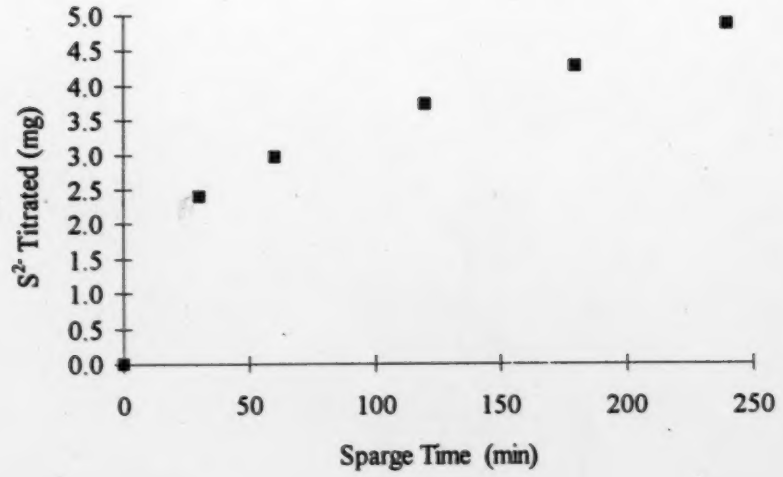

Figure E7. Sulfide Titrated vs. Sparge Time (Digester 6, 7.9 m, May 29 1998).

APPENDIX F. Digester Sulfide Analysis Data

Table F1. Total sulfur tests on digester 3, 7.9 m sludge, May 20 1998 (Control)

Sparge Time (min)	Phosphate Buffer (mL) pH = 6.7	Chemical Addition (mL)	Sulfide Titrated (mg)	Mean (mg)	Total sulfur in liquid portion (mg/L)	Total sulfur in solid portion (mg/Kg)
30	120	0	5.63			
30	120	0	5.64			
30	120	0	5.59			
30	120	0	5.53	5.60	233	260

Table F2. Total sulfur tests on digester 3, 7.9 m sludge, May 20 1998 (Ferrous reagent grade additions)

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ $4H_2O$ (5g/L) (mL)	Sulfide Titrated (mg)	Mean (mg)	Total sulfur in liquid portion (mg/L)	Total sulfur in solid portion (mg/Kg)
30	120	8	1.48			
30	120	8	1.11			
30	120	8	1.23			
30	120	8	1.22	1.26	226	200

Table F3. Total sulfur tests on digester 3, 7.9 m sludge, May 20 1998 (Ferric reagent grade additions)

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_3$ $6H_2O$ (10g/L) (mL)	Sulfide Titrated (mg)	Mean (mg)	Total sulfur in liquid portion (mg/L)	Total sulfur in solid portion (mg/Kg)
30	120	45.5	1.82			
30	120	45.5	1.84			
30	120	45.5	1.90			
30	120	45.5	1.65	1.80	212	220

Table F4. Total sulfur tests on digester 3, 7.9 m sludge, May 20 1998 (Ferrous waste solution additions)

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mg)	$FeCl_2$ Waste Solution (mL)	Sulfide Titrated (mg)	Mean (mg)	Total sulfur in liquid portion (mg/L)	Total sulfur in solid portion (mg/Kg)
30	120	8	2.37			
30	120	8	2.00			
30	120	8	2.01			
30	120	8	1.96	2.09	220	250

Table F5. Total sulfur tests on digester 3, Cone level sludge, May 21 1998 (Ferrous reagent grade additions)

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ $4H_2O$ (5g/L) (mL)	Sulfide Titrated (mg)	Mean (mg)	Total sulfur in liquid portion (mg/L)	Total sulfur in solid portion (mg/Kg)
30	120	8.5	1.58			
30	120	8.5	1.64			
30	120	8.5	1.75			
30	120	8.5	1.87	1.71	199	220

Table F6. Total sulfur tests on digester 3, Cone level sludge, May 21 1998 (Control)

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	Chemical Addition (mL)	Sulfide Titrated (mg)	Mean (mg)	Total sulfur in liquid portion (mg/L)	Total sulfur in solid portion (mg/Kg)
30	120	0	6.75			
30	120	0	6.86			
30	120	0	6.71			
30	120	0	6.74	6.77	221	460

Table F7. Total sulfur tests on digester 3, Cone level sludge, May 21 1998 (Ferrous waste solution additions)

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_2$ Waste Solution (mL)	Sulfide Titrated (mg)	Mean (mg)	Total sulfur in liquid portion (mg/L)	Total sulfur in solid portion (mg/Kg)
30	120	9	2.07			
30	120	9	1.84			
30	120	9	1.82			
30	120	9	1.69	1.86	210	260

Table F8. Total sulfur tests on digester 3, Cone level sludge, May 21 1998 (Ferric reagent grade additions)

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	$FeCl_3$ $6H_2O$ (10g/L) (mL)	Sulfide Titrated (mg)	Mean (mg)	Total sulfur in liquid portion (mg/L)	Total sulfur in solid portion (mg/Kg)
30	120	70	1.64			
30	120	70	1.53			
30	120	70	1.66			
30	120	70	1.41	1.56	185	210

Table F9. Total sulfur tests on digester 3, 7.9 m sludge, June 2 1998 (Control)

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	Chemical Additions (mL)	Sulfide titrated (mg)	Mean (mg)	Total sulfur in liquid portion (mg/L)	Total sulfur in solid portion (mg/Kg)
30	120	0	1.94			
30	120	0	1.84			
30	120	0	1.71			
30	120	0	1.75	1.81	235	910

Table F10. Total sulfur tests on digester 3, 7.9 m sludge, June 2 1998 (Spiked with 25 mg of sulfide)

Sparge Time (min)	Phosphate Buffer pH = 6.7 (mL)	Theoretical amount of sulfide Added (mg)	Sulfide titrated (mg)	Mean (mg)	Total sulfur in liquid portion (mg/L)	Total sulfur in solid portion (mg/Kg)
30	120	25	22.92			
30	120	25	22.92			
30	120	25	22.91			
30	120	25	22.99	22.94	270	900

Table F11. Total sulfur tests on deionized water spiked with various amounts of sulfide, June 2 1998

Volume of deionized water (mL)	Amount of sulfide added theoretically (mg)	Amount of sulfide detected through total sulfur tests (mg/L)
1000	50 mg	56
1000	150 mg	165

Table F12. Sulfide Titrated relative to day-month 1998

Day - Month 1998	Sulfide Titrated (mg/L)
10-Mar	12.29
13-Mar	12.29
16-Mar	5.35
18-Mar	3.74
19-Mar	3.50
26-Mar	3.50
27-Mar	3.57
28-Mar	3.53
31-Mar	4.03
1-Apr	4.96
2-Apr	6.13
3-Apr	6.29
6-Apr	4.06
7-Apr	4.16
8-Apr	5.09
14-Apr	5.94
15-Apr	7.27
17-Apr	6.76
20-Apr	8.99
21-Apr	10.02
22-Apr	11.37
23-Apr	10.87

Table F13. Sulfide Titrated relative to day-month 1998

Day - Month 1998	Sulfide Titrated (mg/L)
27-Apr	9.36
28-Apr	8.92
29-Apr	8.88
30-Apr	9.52
1-May	10.97
4-May	10.64
5-May	13.62
6-May	12.53
7-May	15.92
8-May	15.92
11-May	14.82
12-May	16.04
13-May	17.41
14-May	16.72
15-May	18.26
16-May	12.07
18-May	10.99
20-May	11.20
21-May	13.54
22-May	12.99
28-May	4.596
2-Jun	3.62

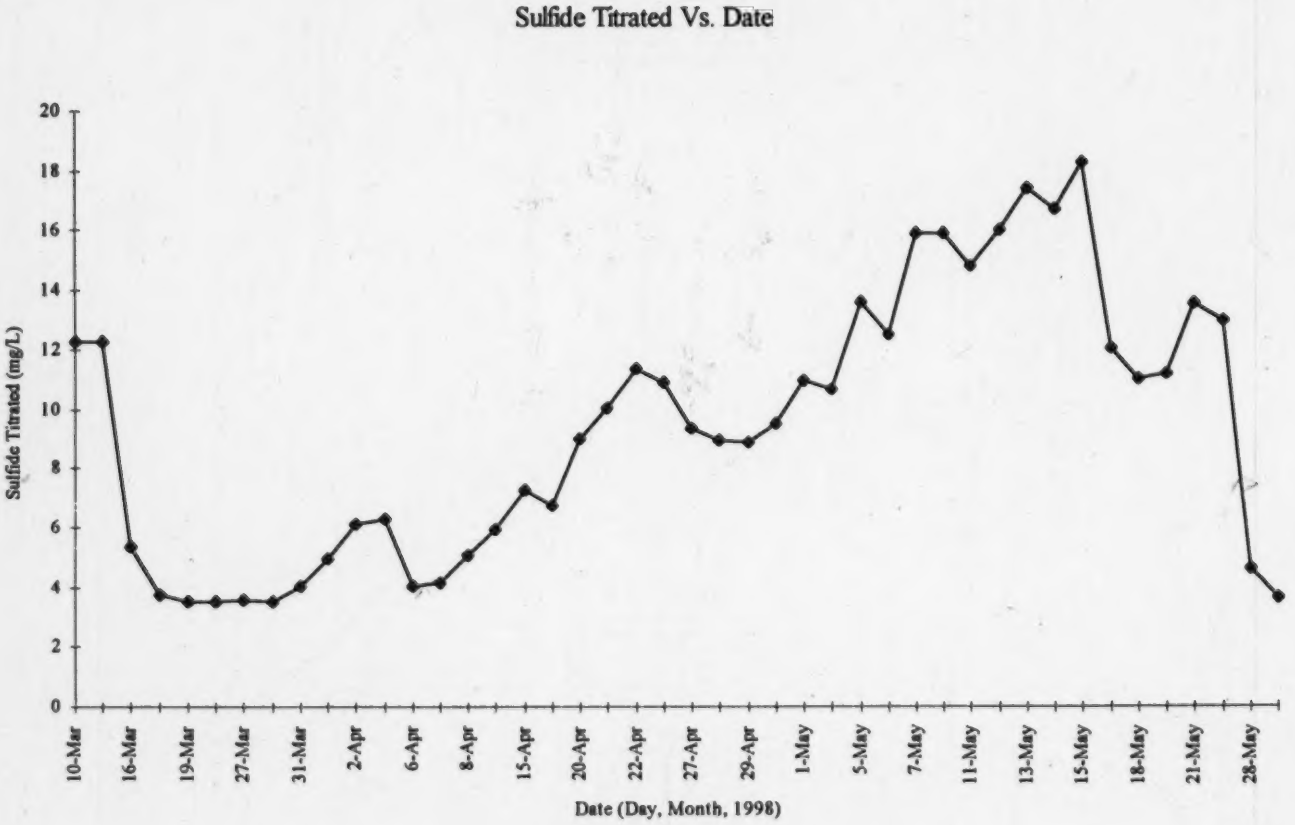

Figure F1. Sulfide Titrated Vs. Date

Table F14. Hydrogen sulfide concentration per month for 1994 to 1997 (historical data)

Month	Average H_2S Concentration (ppm)
January	2746
February	1924
March	711
April	1862
May	2648
June	2068
July	2232
August	3475
September	3532
October	3583
November	3443
December	3307

Table F15. Typical odorous compounds existing in wastewater (Adapted from AIHA, 1989; Amoore et al., 1983; and Sullivan, 1969) (From ASCE and WEF, 1995)

Compound Name	Formula	Detection Threshold, ppm (v/v)
Acetaldehyde	CH_3CHO	0.067
Allyl mercaptan	$CH_2{:}CHCH_2SH$	0.0001
Ammonia	NH_3	17
Amyl mercaptan	$CH_3(CH_2)_4SH$	0.0003
Benzyl mercaptan	$C_6H_5CH_2SH$	0.0002
n-Butyl amine	$CH_3(CH_2)NH_2$	0.080
Chlorine	Cl_2	0.080
Dibutyl amine	$(C_4H_9)_2NH$	0.016
Diisopropyl amine	$(C_3H_7)_2NH$	0.13
Dimethyl amine	$(CH_3)_2NH$	0.34
Dimethyl sulfide	$(CH_3)_2S$	0.001
Diphenyl sulfide	$(C_6H_5)_2S$	0.0001
Ethyl amine	$C_2H_5NH_2$	0.27
Ethyl mercaptan	C_2H_5SH	0.0003
Hydrogen Sulfide	H_2S	0.0005
Indole	$C_6H_4(CH)_2NH$	0.0001
Methyl amine	CH_3NH_2	4.7
Methyl mercaptan	CH_3SH	0.0005
Ozone	O_3	0.5
Phenyl mercaptan	C_6H_5SH	0.0003
Propyl mercaptan	C_3H_7SH	0.0005
Pyridine	C_5H_5N	0.66
Skatole	C_9H_9N	0.001
Sulfur dioxide	SO_2	2.7
Thiocresol	$CH_3C_6H_4SH$	0.0001
Trimethyl amine	$(CH_3)_3N$	0.0004

APPENDIX G. Experimental Procedure and Chemical Preparation

Sludge Sampling Experimental Procedure

1. Collect 500ml of digester sludge at appropriate level (7.9 m or cone level) of digester sampling port. Seal the reactor with pre-made stopper. Pre-made stopper has a luer lok valve, stone diffuser and tubings attached allowing for helium to enter the reactor and digester gases to exit. All tubings and valves are closed.
2. Add 10 mL of 2N NaOH to impinger (Supelco Inc.).
3. Attach tubing (FisherBrand, I.D. 4.8mm, O.D. 7.9mm, Wall Thickness 1.6mm) from the reactor to the helium tank and to the impinger.
4. Add appropriate amount of chemical ($FeCl_2$, $FeCl_3$ or $FeCl_2$ waste solution) to sludge. Using a luer lok syringe and the available teflon valve (Supelco Inc.) for injection.
5. Turn on the magnetic mixer and set to appropriate setting, allowing the sludge and chemical added to mix for 5 minutes.
6. Turn on helium.
7. Add 120 mL of phosphate buffer (pH of 6.7).
8. Allow the helium to purge the digester gases out of the sludge for a total of 30 minutes.
9. Pour contents of impinger into titration cup. Rinse impinger with de-ionized water to wash away any remaining NaOH, again pour contents into titration cup.
10. Titrate sample in titration cup with automatic titrator.

Preparation of Ferrous Chloride Solution

1. Weigh 5 g of $FeCl_2 \bullet 4H_2O$ using an analytical scale.
2. Place ferrous chloride into 1 litre volumetric flask and add 1 litre of de-ionized water.

3. Invert flask to provide a uniform 5g/L $FeCl_2 \bullet 4H_2O$ solution.

Preparation of Ferric Chloride Solution

1. Weigh 10 g of $FeCl_3 \bullet 6H_2O$ using a analytical scale.
2. Add the 10 g of $FeCl_3 \bullet 6H_2O$ into a 1 litre volumetric flask and fill with 1 litre of de-ionized water.
3. Invert flask to provide a uniform 10g/L $FeCl_3 \bullet 6H_2O$ solution.

Preparation of Ferrous Chloride Waste Product Stock Solution

1. Pipette 5 mL of concentrated waste product into 500 ml volumetric flask.
2. Add 495 mL of de-ionized water.
3. Invert flask to provide a uniform ferrous chloride waste solution.

Preparation of 2N NaOH Solution

1. Measure 200ml in a graduated cylinder of 10N NaOH aqueous solution.
2. Add 200 ml of NaOH solution into a 1 litre volumetric flask.
3. Fill volumetric flask to 1 litre mark with deionized water.
4. Invert flask with to provide a uniform 2N NaOH solution.

Preparation of Phosphate Buffer

1. Measure 452 mL of 0.4 M $NaH_2PO_4 \bullet H_2O$ in graduated cylinder.
2. Measure 500 mL of 0.4 M Na_2HPO_4 in graduated cylinder.
3. Add 452 mL of 0.4 M $NaH_2PO_4 \bullet H_2O$ and 500 ml of 0.4 M Na_2HPO_4 into a 1000 ml beaker. Stir to provide adequate mixing.
4. Add contents of beaker into a 1000 ml volumetric flask.

Mettler Toledo DL53 Automatic Titrator V1.0 Input Values

Title	
Method I.D.	9999
Sample	
Sample I.D.	H_2S
Entry Type	Volume
Lower Limit (mL)	0.0
Upper Limit (mL)	50.0
Molar mass M	32.06
Equivalent number z	2
Titration Stand	Stand 2
Temperature Sensor	Manual
Stir	
Speed (%)	50
Time (s)	5
EQP titration	
Titrant/Sensor	
Titrant	$AgNO_3$
Concentration (mol/L)	0.05
Sensor	DM141
Unit of meas.	mV
Predispensing	to volume
Volume (mL)	0.0
Titrant Addition	Dynamic
ΔE (set)(mV)	4.0
ΔV(min) (mL)	0.04
ΔV(max)(mL)	2.0
Measure mode	Equilibrium controlled
ΔE (mV)	0.5
Δt (s)	1.0
t (min) (s)	4.0
t (max) (s)	20.0
Recognition	
Threshold	200
Steepest Jump	No
Range	No
Tendency	None
Termination	
at maximum volume (mL)	5.0
at potential	No
at slope	No
after number EQPs	Yes
n =	4
comb. termination conditions	Yes

Evaluations	
Procedure	Standard
Potential 1	No
Potential 2	No
Stop for reevaluation	No
Calculation	
Formula	R=VEQ
Constant	
Decimal places	4
Result unit	mL
Result name	Eq. Point Vol.
Statistics	No
Calculation	
Formula	R2=Q*C2
Constant	C2=M/z
Decimal Places	3
Result unit	mg
Result name	S^{2-} Conc.
Statistics	No
Calculation	
Formula	
Constant	
Decimal Places	0
Result unit	
Result name	
Statistics	No
Report	
Output Unit	Printer
Results	Yes
All Results	No
Raw Results	No
Table of measured values	No
Sample data	No
E - Vcurve	Yes
$\Delta E/\Delta V$ - V curve	No
$\Delta^2 E/\Delta V^2$ - V curve	No
log $\Delta E/\Delta V$ - V curve	No
E - t curve	No
V - t curve	No
$\Delta V/\Delta t$ - t curve	No

APPENDIX H. Floc Size and Diffusion Rate Analysis

Table H1. Floc dimensions for digester 6, 7.9 m sludge, S^{2-} concentration = 2.02 mg

Floc	Approximate Length (mm)	Approximate Width (mm)
1	0.232	0.058
2	0.290	0.058
3	0.116	0.058
4	0.174	0.116
5	0.116	0.058
6	0.145	0.116
7	0.348	0.087
8	0.116	0.058
9	0.203	0.058
10	0.058	0.058
11	0.174	0.058
12	0.174	0.145

Average width = 0.077 mm
Average length = 0.179 mm
Average Cross sectional Area = 0.014 mm^2
Average Total Surface Area = 0.0374 mm^2

Table H2. Floc dimensions for digester 3, 7.9 m sludge, S^{2-} concentration = 3.38 mg

Floc	Approximate Length (mm)	Approximate Width (mm)
1	0.232	0.232
2	0.116	0.116
3	0.174	0.116
4	0.232	0.232
5	0.174	0.058
6	0.463	0.232
7	0.174	0.116
8	0.174	0.116
9	0.232	0.058
10	0.405	0.116
11	0.174	0.116
12	0.174	0.058

Average width = 0.130 mm
Average length = 0.227 mm
Average cross sectional area = 0.030 mm^2
Average total surface area = 0.0759 mm^2

Table H3. Floc dimensions for digester 3, 7.9 m sludge, S^{2-} concentration = 8.36 mg

Floc	Approximate Length (mm)	Approximate Width (mm)
1	0.174	0.145
2	0.348	0.087
3	0.463	0.116
4	0.116	0.116
5	0.348	0.174
6	0.232	0.174
7	0.521	0.116
8	0.174	0.174
9	0.116	0.116
10	0.087	0.087
11	0.174	0.087
12	0.232	0.145

Average width = 0.128 mm
Average length = 0.249 mm
Average cross sectional area = 0.032 mm^2
Average total surface area = 0.0794 mm^2

Table H4. Floc dimensions for digester 3, 7.9 m sludge, S^{2-} concentration = 5.34 mg

Floc	Approximate Length (mm)	Approximate Width (mm)
1	0.116	0.116
2	0.232	0.058
3	0.348	0.058
4	0.174	0.058
5	0.116	0.058
6	0.174	0.087
7	0.087	0.087
8	0.174	0.058
9	0.087	0.087
10	0.174	0.116
11	0.203	0.087
12	0.116	0.058

Average width = 0.077 mm
Average length = 0.167 mm
Average cross sectional area = 0.013 mm^2
Average total surface area = 0.0300 mm^2

Table H5. Floc dimensions for digester 6, 7.9 m sludge, S^{2-} concentration = 2.41 mg

Floc	Approximate Length (mm)	Approximate Width (mm)
1	0.116	0.058
2	0.232	0.116
3	0.116	0.058
4	0.348	0.116
5	0.116	0.087
6	0.174	0.058
7	0.116	0.058
8	0.232	0.058
9	0.174	0.058
10	0.174	0.058
11	0.145	0.058
12	0.348	0.174

Average width = 0.080 mm
Average length = 0.191 mm
Average cross sectional area = 0.015 mm^2
Average total surface area = 0.0462 mm^2

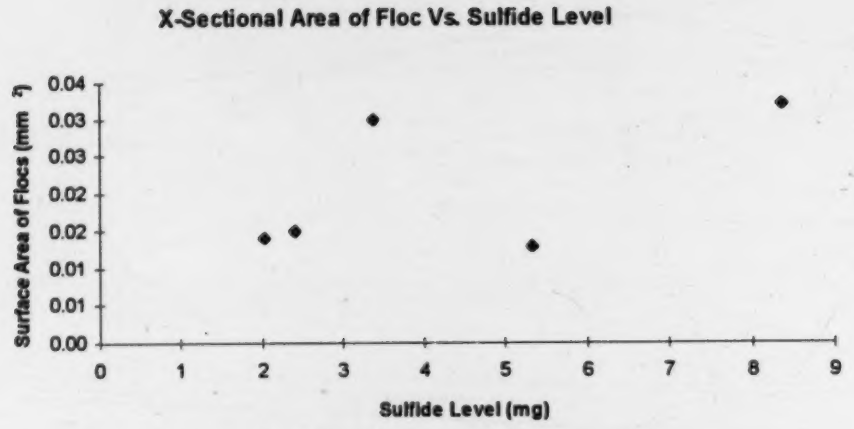

Figure H1. Relationship between cross-sectional area and sulfide level.

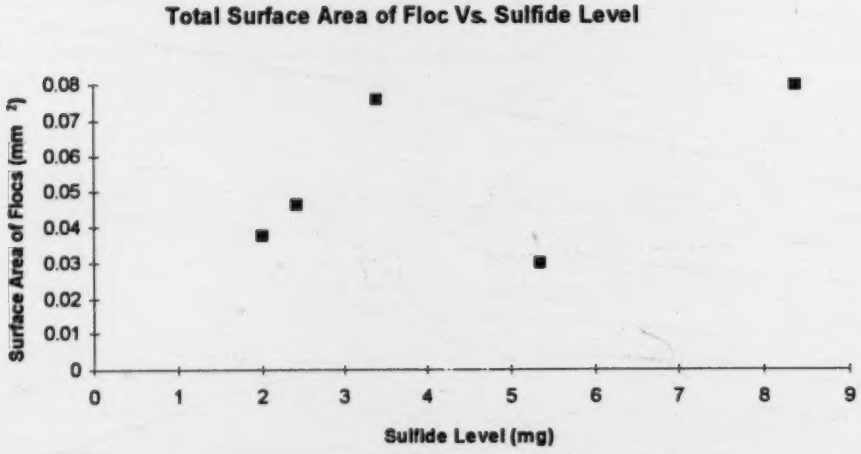

Figure H2. Relationship between surface area of floc and sulfide level.

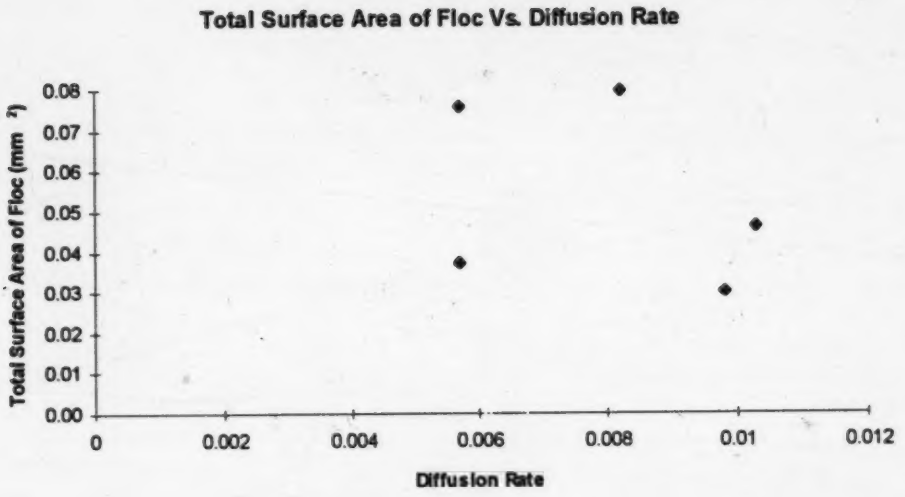

Figure H3. Relationship between total surface area of floc and diffusion rate.

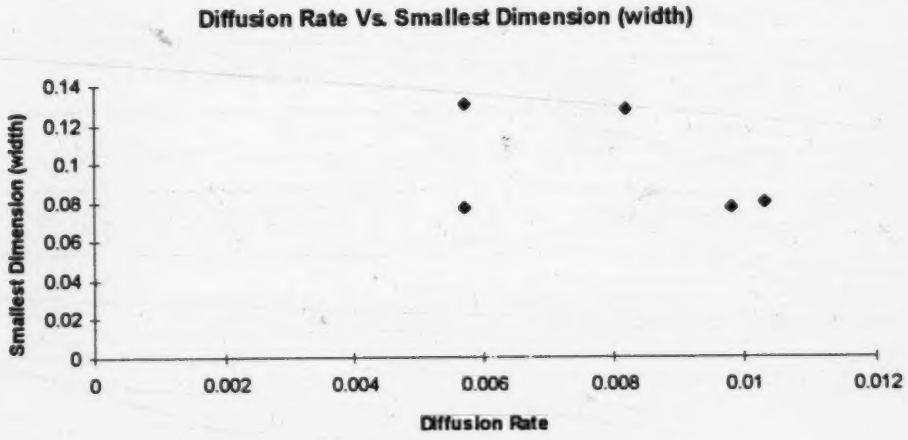

Figure H4. Relationship between floc width and diffusion rate.